

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-302176

(43)Date of publication of application : 16.11.1993

(51)Int.Cl. C23C 26/00
B05D 1/24

(21)Application number : 03-224782

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(22)Date of filing : 09.08.1991

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(54) METHOD FOR FORMING COATING FILM

(57)Abstract:

PURPOSE: To apply a powdery coating film excellent in corrosion resistance and adhesive strength on various members by vibrating or agitating a member to be treated, an unhardened resin, a powdery material and a coating film forming medium in a vessel.

CONSTITUTION: The member to be treated, the resin, the powder material and the coating film forming medium are charged into the vessel. The resin is in partially unhardened state at the initial stage of the coating film forming process and is composed of e.g. melamine resin, epoxy resin, urethane resin or the like. The powdery material is the structural material of the powdery coating film formed on the member to be treated and composed of e.g. various metals, a powdery ceramic, a plastics or the like. And the coating film forming medium is smaller than the member to be treated and larger than the powdery material. And the resin is hardened while vibrating or agitating the member, the resin, the powder and the medium charged into the vessel.

LEGAL STATUS

[Date of request for examination] 18.12.1997

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 2991544

[Date of registration] 15.10.1999

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] In the approach of sticking and forming a coat in a processed member front face A processed member, The resin like a coat formation fault which is in the condition of not hardening, partially in the first stage at least, The fine-particles matter (it sets like a coat formation fault and there is also a thing of hard resin powder rather than said resin), And the coat formation approach characterized by forming the coat which contains the fine-particles matter when a dimension is substantially smaller than said processed member and a dimension adds vibration or stirring to a large coat formation medium within a container substantially rather than said fine-particles matter.

[Claim 2] it is serially about said processed member, the fine-particles matter, and resin, putting in a coat formation medium beforehand in said container, and adding vibration or stirring -- it is -- the coat formation approach according to claim 1 characterized by inserting in said container at coincidence.

[Claim 3] The coat formation approach given in two from claim 1 characterized by stiffening said resin during vibration or stirring.

[Claim 4] The coat formation approach given [to claims 1-3 characterized by mixing a coat formation medium, said processed member, and resin within said container, inserting the fine-particles matter in said container further, and performing vibration or stirring] in any 1 term.

[Claim 5] The processed member which gave the coat which consists of the first resin like a coat formation fault which is in the condition of not hardening, partially in the first stage at least in the approach of sticking and forming a coat in a processed member front face, The fine-particles matter (it sets like a coat formation fault and there is also a thing of hard resin powder rather than said resin), And the coat formation approach characterized by forming the coat which contains the fine-particles matter when a dimension is substantially smaller than said processed member and a dimension adds vibration or stirring to a large coat formation medium within a container substantially rather than said fine-particles matter.

[Claim 6] The coat formation approach according to claim 5 which is said first resin and congener, or resin of a different kind, and is characterized by mixing with said processed member, the fine-particles matter, and a coat formation medium the second resin like a coat formation fault which is in the condition of not hardening, partially in the first stage at least.

[Claim 7] The coat formation approach given in any 1 term to claims 1-6 characterized by hardening the resin after coat formation and in this coat on said processed member front face.

[Claim 8] The coat formation approach given [to claims 1-7 characterized by removing the isolation fine-particles matter which remains after coat formation on said processed member front face at the surface section of this coat] in any 1 term.

[Claim 9] The coat formation approach according to claim 8 characterized by rubbing the processed member front face in which this coat was formed, by the elastic medium in case the residual isolation fine particles of said coat surface section are removed.

[Claim 10] The coat formation approach given [to claims 1-9 characterized by heat-treating to the processed member in which said coat was formed] in any 1 term.

[Claim 11] the same as that of said resin in the processed member in which said coat was formed -- it is -- it is -- the coat formation approach given [to claims 1-10 characterized by covering with different resin from said resin] in any 1 term.

[Claim 12] The coat formation approach according to claim 11 characterized by a dimension adding vibration or

churning to a small coat formation medium and this resin within a container substantially rather than said processed member in case resin covering according to claim 11 is given.

[Claim 13] The coat formation approach according to claim 11 characterized by performing resin covering according to claim 11 by paint.

[Claim 14] The coat formation approach given [to claims 1-10 characterized by forming the coat of a metal or an alloy in the processed member which formed said coat using the conductive fine-particles matter] in any 1 term.

[Claim 15] The coat formation approach according to claim 14 characterized by forming the coat of said metal or an alloy with electroplating or nonelectrolytic plating.

[Claim 16] The coat formation approach given [to claims 1-15 characterized by said processed member being a rare earth sintered magnet] in any 1 term.

[Claim 17] The coat formation approach given [to claims 1-16 characterized by said processed member being a rare earth resin bond magnet] in any 1 term.

[Claim 18] The coat formation approach given [to claims 1-17 characterized by replacing with some or all of resin with which vibration or stirring is added, and using the inorganic adhesion matter with said processed member, said fine-particles matter, and a coat formation medium] in any 1 term.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the approach of forming a coat in the front face of various members. The various members said here are the machine part used for various machines, an automobile and other cars, a vessel, an airplane, etc., the electrical and electric equipment and electronic parts, an ornament supply, metallic ornaments, a magnet, toy components, etc., and are bits and pieces comparatively. Moreover, the quality of the materials of a member are a metal, an alloy, an intermetallic compound, an inorganic compound, plastics, the ceramics, etc. Moreover, various well-known coats are already formed in the front face, or, as for various members, surface treatment may be given.

[0002] Moreover, the "coat" formed by the approach of the invention in this application aims at formation of the substrate layer for forming various, still better known coats for the purpose of corrosion prevention, mechanical-strength grant, the insulating stratification, and/or fine sight grant. A lubricative application [****] does not make this invention an object with a wear-resistant application [****], molybdenum disulfide, etc. with titanium nitride etc.

[0003]

[Description of the Prior Art] Furthermore, this invention relates to amelioration of the approach of forming the coat of fine particles. As a conventional technique which forms the coat of fine particles, the following approaches are well-known.

[0004] ** A powder coating this gentleman method is an approach of depositing powder coatings on the member which carried out preheating by spraying, spraying, thermal spraying, etc., they carrying out melting to it, and obtaining a paint film. Since this approach does not use a solvent, it does not have a public nuisance by the solvent, and has the advantage which is saving-resources-like. As patent reference about this approach, there are JP,2-258084,A, JP,57-13347,B, JP,53-29347,A, and JP,58-37029,B. Moreover, powder coating is performed by electrostatic spray painting.

[0005] ** A fine-particles covering this gentleman method is divided into that in which the processed member front face has an adhesive property, and the approach of being a non-adhesive property. According to JP,2-71872,A belonging to the former, the fine-particles matter is contacted on the member front face which gave adhesiveness beforehand, the fine particles which added vibration to the member and adhered to the member front face are compressed below into bulk density, and the method of removing the powder which has not fixed to the posterior part material is indicated. As a member, the fluorescence toner is shown for the screen of color television in said official report as an example as fine particles.

[0006] JP,52-43731,A belonging to the latter puts in a metal or alloy powder, and the spherical or granular hard matter in metal goods in the air, rotates or vibrates these metal goods, and indicates the approach of covering a metal or alloy powder to a product inside. Fine particles are stuck to metal goods by pressure, and diffused junction is also performed by making diffusion cause between a powdered metal and the metal of a product with the heat energy which originates in vibration at coincidence. According to this approach, it is stated that the thermal resistance of the inside of a hollow product improves.

[0007] ** It is the approach of making the metal powder rolling-out method metal powder adhere on the surface of a rolled plate, sticking powder to a rolled plate by pressure with roll rolling, and carrying out diffused junction by the postheat treatment (refer to JP,52-33840,A, No. 143531 [51 to], No. 54270 [57 to], and 47 No. -29232).

[0008]

[Problem(s) to be Solved by the Invention] The formation approach of a fine-particles coat has the following advantages to the various coat forming methods. In order not to use :acid, alkali, etc. to electroplating or a nonelectrolytic plating method, while processing of processing waste fluid becomes unnecessary, even if a processed member is activity, problems, such as corrosion, do not arise.

Exposing :processed member to an elevated temperature to a hot-dipping method is avoided.

PVD and a CVD method -- receiving -- : -- large-scale equipment has needlessness and high productivity.

[0009] However, it is required to satisfy the engine performance required of a coat for applying a fine-particles coat to various members, and also for the efficiency and dependability of the coat forming method to be high.

[0010] ** Since the metal powder rolling-out method is restricted to the quality of the material which a processed member is a plate and can be rolled out, a direct fine-particles coat cannot be formed in a machine part etc.

[0011] ** It cannot be said that it is efficient since the powder coating approach needs actuation of reversing or hanging it to ** etc. when processed members are accessories although it applies powder coatings to a processed member with spraying of a coating, a spray, etc. Moreover, there is a problem of being inapplicable in an ingredient with degradation of the quality of the material by heating a processed member etc.

[0012] ** Since powder was compressed by vibration between powder particles in the powder which is on it although it has a certain amount of [the fine particles in which the approach indicated by JP,2-71872,A among fine-particles coating adhered to the adhesive front face] adhesion force, when fine-particles covering requires external force, since there are also many dedropping and clearances where it becomes empty and a corrosive medium permeates easily, don't turn to the purposes, such as corrosion prevention. Furthermore, when a processed member has irregularity, the fine particles to a crevice are attached and the surroundings are poor.

[0013] ** The approach indicated by JP,52-43731,A among fine-particles coating performs mechanical association (sticking by pressure) and diffused junction to coincidence. For that, considerable energy is required, for example, the high-speed planetary mill of the vibration mill of 500kg of exciting force or rotational frequency 300rpm is used in the example. Therefore, a processed member needs for reinforcement to be high and neither a ceramic nor the plastics with low reinforcement serves as a processed member. Moreover, since weak fine particles, such as an oxide, are destroyed by vibration, it is inapplicable.

[0014] The approach indicated by above-shown JP,52-43731,A is not employable as the approach of forming a coat in the various members which can apply only to covering of only an inside, and are said by this invention since considerable high energy is required. ** Although application to various members is possible for the approach of JP,2-71872,A among the powder coating approach and fine-particles coating of **, since there are the above problems, this invention aims at offering the coat formation approach which adhesion force is excellent in and can form a precise fine-particles coat while it raises the efficiency of fine-particles covering formation.

[0015]

[Means for Solving the Problem and its Function] In the fine-particles coat forming method in this invention method, the features-place is in below compared with a conventional method. If resin, the fine-particles matter, and a processed member are vibrated or stirred within a container with a coat formation medium, the layer of resin will be first formed in a processed member front face. Since contact of a member front face, resin, and a member front face and a fine-particles particle takes place to coincidence when the thickness of this resin layer changes by the order of materials charging of the fine-particles matter, resin, a coat formation medium, and a processed member, or the mixed method, for example, an injection of resin and the fine-particles matter is performed to coincidence, it may become [whether the resin independent layer formed in a member front face becomes very thin, and] detection difficulty.

[0016] Resin coat formation is followed, and the fine-particles matter is caught and fixed by the resin layer according to the adhesion of a resin layer. When a resin layer hardens on a processed member front face similarly, the fine-particles matter is caught and hardened. Since the coat formation medium which has received vibration or stirring is pressed fit between the particles which gave striking power to the fine-particles matter which has received vibration or stirring similarly, were caught by the resin layer and were already stuffed into it in the particle of said fine-particles matter, in addition to the adhesion of resin etc., the fine-particles matter is fixed still more strongly by the striking power of a coat formation medium. Moreover, a collision of a processed

member comrade also takes place in part, and press fit of the fine-particles matter is promoted similarly. Therefore, since a resin layer also becomes thick while many fine-particles matter comes to be gradually mixed by the resin layer, a coat continues growing.

[0017] Since association is made between resin and the fine-particles matter and also the particle comrade of the fine-particles matter collides on a processed member front face through the striking power of a coat formation medium as explained above, the bonding strength by diffusion between atoms by frictional heat is mainly secondarily made by plastic deformation and the row also among these. Especially when the fine-particles matter is the metal which is rich in ductility like aluminum, Cu, Zn, Sn, Au, Ag, Pb(s), and these alloys, an alloy, or plastics, these powder particle that collided deforms plastically and it is joined like a pressure welding. Moreover, such junction takes place also between the fine-particles matter and a processed member. As a result, the configuration of the matter in a coat becomes firm. The coat stratification according that the fine-particles matter is inductility matter to association between fine-particles particles and this stops being able to happen easily.

[0018] The coat formation medium which collides with a coat front face presses out resin from between the particles of the fine-particles matter, and oozes on the coat front face under formation. Resin adheres also to a coat formation medium in part. the processed member front face of others [resin / this / medium / coat formation] -- the time -- colliding -- the time -- again -- a processed member front face -- adhering . A fine-particles particle adheres to this resin layer front face. The extraction of such resin and the above-mentioned coat growth advance to coincidence. However, the rate of the fine-particles matter in a coat front face increases with membranous growth. then, a coat formation medium deals a blow to the fine-particles matter in a coat front face -- while coming out, and condensing the fine-particles matter and the rate of resin decreasing increasingly, a growth-of-anodic-oxide-film rate falls. This is because the adhesion force in that the fine-particles matter is omitted from a coat and a surface becomes low.

[0019] this invention approach explained above is an approach that the coat in which was characterized by using the striking power of the coat formation medium carried although it does not participate in coat formation as compared with above-shown JP,2-71872,A, and adhesive strength was excellent by this can be obtained. Moreover, it is the approach that this invention approach is formed by the resin which mixes an adhesion side together with other coat formation mixture as compared with above-shown JP,52-43731,A, and it is characterized by using the striking power of the coat formation medium carried although it does not participate in coat formation, and practically sufficient adhesive strength is excellent in little energy by this, and a precise coat can be obtained.

[0020] Condition (a) - (d) required in order to realize like the above coat formation faults is explained.

(a) Locally or on the whole, resin needs to be in the condition of not hardening, in the first stage, even if few [like a coat formation fault]. If it is in the condition which the whole resin hardened [whole / coat formation fault] For example, formation of the resin layer in the processed member front face which serves as a forerunner of coat growth since there is almost no adhesive strength on the front face of a member of resin when the solid-state resin hardened completely is independently used in ordinary temperature does not take place. Moreover, since [of a between / fine-particles particles] it does not happen beginning to bleed, resin, the fine-particles matter, a processed member, and a coat formation medium (hereafter, when naming generically, "coat formation mixture" is called) stop at only being mixed. "Un-hardening" means that it is in an elastic condition rather than the resin in the phase which evaporation, curing, etc. of a solvent are completed to the resin in a coat, and is finally used.

[0021] (b) It is necessary to include a processed member and coat formation mixture needs to be made to vibrate or stir. If a processed member is made to contact, fixing a processed member and mixing other coat formation mixture, it will become difficult to make a uniform coat form all over a processed member. Moreover, a coat formation medium is made to secede from a processed member front face by mixing, and although an intervention is carried out to coat formation, it can stop at a medium.

[0022] (c) Although a coat formation medium generates striking power and formation of a coat is carried, it does not become the component of a coat substantially in itself. Since a coat formation medium will be caught in a coat if a larger coat formation medium than a processed member cannot generate uniform striking power on the former front face and it is smaller than powder, the requirements for a dimension which was limited to claim 1 are required. However, as long as it is 70% or less of range in a volume ratio, the bigger medium than a

processed member may be contained. Moreover, when the direction on which striking power is centralized to some extent uses a spherical medium since press fit of fine particles advances well for example, the diameter is more desirably desirable 1mm or more 0.5mm or more, and, also in other configurations, it applies to this. Moreover, when smaller [than a processed member] and each of media is replaced with the ball of this volume, it says that the diameter is smaller than the greatest thing among the diameters of a processed member. Moreover, if requirements are filled with the average dimension to powder, desired striking power can be made. That is, if the former is larger than the latter with an average dimension in a part of particle used as a coat formation medium being finer than the fine-particles matter, desired striking power can be made. However, it is desirable for a medium finer than these fine-particles matter to have a possibility that it may be crowded for the inside of a coat, and not to be contained as much as possible.

[0023] The quality of the material of a coat formation medium needs to be satisfying the following requirements.

** There needs to be no big form status change-ization which observes a coat formation medium before and after coat formation by plastic deformation, and is accepted with the naked eye, and set like a coat formation fault and elastic deformation should not become extremely large. Therefore, soft rubber etc. does not satisfy this requirement.

** It is divided and there are not a chip, rapid wear, etc. (there may be some wear by long-term use).

[0024] If the coat formation medium of the quality of the material which does not satisfy these requirements causes plastic deformation by the collision with processed material or causes extremely big elastic deformation like soft rubber, the blow dealt to the latter will be insufficient and desired coat formation will not take place. Moreover, if it is divided and a chip and rapid wear take place, the useful life longevity of a medium becomes short and is uneconomical.

[0025] (d) The fine-particles matter must be smaller than a coat formation medium, in order to be incorporated in a coat. Although especially the property of the fine-particles matter is not limited, in the case of resin powder, it is required to be resin more nearly hard than the resin which set like the coat formation fault and was stated by (a). Hereafter, each claim is explained about the configuration and operation in order.

[0026] This invention which consists of above-mentioned requirements (a) - (d) In the approach of sticking and forming a coat in a processed member front face A processed member, The resin like a coat formation fault which is in the condition of not hardening, partially in the first stage at least, The fine-particles matter (it sets like a coat formation fault and there is also a thing of hard resin powder rather than said resin), And when a dimension is substantially smaller than said processed member and a dimension adds vibration or stirring to a large coat formation medium within a container substantially rather than said fine-particles matter, it is the coat formation approach characterized by forming the coat containing the fine-particles matter (claim 1).

[0027] In this invention as resin Melamine resin, an epoxy resin, phenol resin, Furan resin, urethane resin, an unsaturated polyester resin, polyimide resin, The thermosetting resin of 1 liquid, such as a urea-resin, or 2 liquid hybrid model, unsaturated polyester, Ultraviolet rays, such as an acrylic monomer with partial saturation poly isocyanate and a hydroxyl group, The resin hardened by the electron ray and other radiation irradiation, acrylic resin, polyester, Polyethylene, polyethylene terephthalate, polypropylene, a polyvinyl chloride, Thermoplastics, such as polyvinyl alcohol, nylon, polystyrene, and polyvinyl acetate, and those liquefied prepolymers or a monomer and the organic binder generally used for powder molding, for example, paraffin, camphor, etc. can be used. Moreover, natural products, such as gelatin, glue, and a Rhus verniciflua, can be used as resin.

[0028] Moreover, since resin needs to spread round the front face of a processed member at homogeneity, the above-mentioned resin has the most desirable thing that is not half-liquid-like hardened [liquefied or].

Moreover, a fluidity is raised, and in order to spread over a member front face at homogeneity, an organic solvent or water can use a solid-state or liquefied resin, dissolving, diluting or distributing. In this case, since a solvent or water evaporates during mixing, adhesiveness increases gradually, and adhesion of fine particles takes place. However, if there are too many amounts of an organic solvent etc., it will become inadequate adhering to the processed member front face of the fine-particles matter. Moreover, thermoplastics is heated, increases a fluidity and adhesiveness and can be used. Since the fluidity of resin becomes small when using it independently without distributing fine-particles resin to a solvent etc., in order to distribute homogeneity between fine-particles particles, it is desirable to fine-particles be the matter, to be an EQC, or for fine-particles resin to be more detailed. These solvents, water, etc. are evaporated under coat formation and from the coat

after formation.

[0029] Furthermore, when a processed member contains resin like a resin bond magnet and a plastics member, add the solvent of the resin into coat formation mixture, resin is made to begin to melt from a processed member, and coat formation mixture can also be supplied. If the viscosity of resin is raised by evaporation of a solvent etc., the resin which once began to melt will adhere to a processed member, and will form a resin coat.

[0030] Next, the fine-particles matter is a constituent of the fine-particles coat formed on a processed member. If it is resin, plastics, coating powder, etc. further and is various metals, alloy powder and ceramic powder, and the thing that has functions, such as corrosion prevention, fine sight grant, insulating grant, and improvement in on the strength, as fine-particles matter, various fine particles can be used.

[0031] If an example is given, as metal powder, there is alloy powder which makes a principal component powder, such as aluminum, Cu, Mg, Ti, Fe, Cr, Co, nickel, Zn, Pb, Sn, Rh, Ir, Pd, Pt, Ag, Au, Mo, and W, and them. All of these metals excel resin in reinforcement, and since there is little deterioration by water, salt water, etc., corrosion resistance is excellent. Since stainless steel, Cr, nickel, Mo, W, etc. make the firm passive state film on a front face, it excels in corrosion resistance. Therefore, these metals raise the reinforcement of a coat, and corrosion resistance. Since Rh, Ir, Pd, Ag, Au, etc. have a good fine sight and corrosion resistance when the place by which each metal is characterized is mentioned, these properties are given to a coat. Moreover, since Cu etc. has good corrosion resistance and good electrical conductivity, it is used for formation of an anticorrosion coat, formation of a plating primer coating layer, etc. good. nickel is also used for formation of a plating primer coating layer etc. good. Zn and Sn carry out the corrosion prevention of almost all the metals according to the sacrificial anode effectiveness.

[0032] Ceramic powder is chemically more stable than a metal, and corrosion resistance is superior to the above-mentioned resin-metal compound coat. various kinds, such as a multiple oxide which makes the base an oxide, MgO and aluminum $2O_3$, SiO_2 , TiO_2 , CrO_2 , MnO_2 , Fe_2O_3 , FeO , Fe_3O_4 , CoO , NiO , CuO , ZnO and ZrO_2 , MoO , and them as these ceramics, and TiN , BN , -- various kinds, such as SiC , WC , $TiC(s)$, etc., such as a stable nitride, -- stable carbide etc. can be used.

[0033] The above-mentioned metal, the above-mentioned ceramics, etc. may be contained in resin as a compounding agent, a pigment, etc. Moreover, two or more sorts of powder may be mixed and used.

[0034] When using resin powder as fine-particles matter, the powdered resin which made various thermosetting resin, **** plasticity resin, and these distribute various pigments can be used. Therefore, since the coat of powdered resin has leather **** and good adhesion in the condition of carrying out full hardening and it excels in corrosion resistance as a result, in this invention, liquefied resin and powdered resin may be kneaded with other coat formation mixture.

[0035] The grain size of the fine-particles matter changes according to the magnitude of a processed member, the thickness of a coat, and the quality of the material of the fine-particles matter. In the case of the fine particles which cannot deform easily due to hard [, such as ceramic fine particles,], it is desirable for grain size to be small, and in the case of the metal powder which is rich in ductility, although it may be larger than this, generally, it is within the limits of 0.05-500 micrometers. 0.1-300 micrometers is within the limits of 0.1-100 micrometers more desirably. Generally, fine particles are easy to be caught with resin, so that grain size is small. Moreover, the particle with a small grain size tends to be pushed in by blow between the particles of the fine-particles matter currently distributed on a resin coat, and sticking by pressure and association with the fine-particles comrade or processed ingredient by plastic deformation tend to take place. Therefore, striking power is so small that the grain size of the fine-particles matter is small, and it ends, and the surface roughness of a coat also becomes small.

[0036] A coat formation medium can use a rigid plastic etc. for products made from the ceramics, such as iron, carbon steel, other alloy steel, copper and a copper alloy, aluminum and an aluminium alloy, other various metals, the product made from an alloy or aluminum $2O_3$, SiO_2 , TiO_2 , ZrO_2 , and SiC , and a glass pan. Moreover, hard rubber can also be used if sufficient striking power for coat shaping is applied. It is necessary to choose suitably the size of these media, and the quality of the material according to the quality of the material of the configuration of a member and size, and the fine particles to be used. Moreover, two or more sizes and the medium of the quality of the material can also be mixed and used. Moreover, they can also use depending on the case, being able to give surface treatment and surface coating. Moreover, the compound medium constituted with two or more above-mentioned ingredients may be used. Moreover, since relaxation and equalization of

striking power are performed and the homogeneity of a coat and dispersion of thickness are suppressed, elastic media, such as wood flour, and soft rubber, flexible plastics, may be suitably mixed in 50% or less of range of a volume ratio to said medium. Since these hardly produce striking power if they are independent, they are surely used together with said coat formation medium.

[0037] A globular shape, an ellipse form, a cube, the triangle pole, a cylinder, a cone, a triangular pyramid, a square drill, rhombohedron, an indeterminate form object, and other various configurations can be used for the configuration of a coat formation medium.

[0038] The rate of each component (element) of coat formation mixture determines that it does not incline toward one of elements, but the whole balances so that an operation of a request of each component may be demonstrated. The amount of fine particles and resin becomes settled with the sum total of the thickness of the coat given to a member, and the surface area of a member. However, as for the ratio of resin and fine particles, it is desirable to convert into the volume after hardening of resin and to set up a pitch to 0.5% or more. Adhering to the member of fine particles becomes being less than [this] inadequate. moreover, the mixing ratio of a medium and a member -- although it changes with configurations of a member, if a medium is not blended 20% or more by the apparent volume ratio at least, it is difficult for a rate for the homogeneity on the front face of a member and sufficient blow not to be performed, but to obtain a good coat.

[0039] Vibration or stirring within a container can be carried out by various approaches which are described below. the arm 3 (refer to drawing 1) which was prepared in the container 2 and fixed to the revolving shaft 4, and the wing 5 (refer to drawing 2) which fixed to the revolving shaft 4 -- or although not illustrated, it is accomplished with agitators, such as an impeller and a blade. In addition, ten in drawing is coat formation mixture. Moreover, as shown in drawing 3 , the drum or pot-like container itself may be rotated on a roller 6. As furthermore shown in drawing 4 , the drum-like container 2 which fixed to the revolving shaft may be rotated. The upper part may be released, the container may be sealed, or whichever is sufficient as it. In addition, a container 2 may be shaken as shown in drawing 5 . You may agitate during rocking. Moreover, the powder mixture 10 may be put in in the container 2 attached at the tip of the arm 7 which fixed symmetrically to the revolving shaft 4 shown in drawing 6 R> 6, and powder mixture may be mixed with a centrifugal force. It is desirable to make a container 2 rotate. As long as actuation of a container is the same, a rotational device may use the electrode holder of not only this but the shape for example, of a disk.

[0040] Or vibration may be added to coat formation mixture with the shaker 8 prepared in a container 2 and out of the container (refer to drawing 7). The magnitude of the force (exciting force) which takes an example to the approach of adding vibration below, and is applied to coat formation mixture is explained. The value (henceforth "exciting-force-ed"-dimensionless number -) which averaged exciting force by the gravity (henceforth "oscillating gravity") of a container and coat formation mixture becomes the index of the impulse force which a coat formation medium applies to a processed member. As an example, when it is weight-1kgf of a 2.8l. container, weight-10kgf of a steel ball (coat formation medium), and weight-1kgf of a processed member, oscillating gravity serves as 12kgf(s). At this time, the exciting force with the desirable period of 40Hz is 20-50kgf. Therefore, exciting force-ed is set to $1.67 (= 20/12)$ - $4.17 (50/12)$.

[0041] When using a larger container and it is weight-4.5kgf of a 20l. container, weight-70kgf of a steel ball (coat formation medium), and weight-5.5kgf of a processed member as an example, oscillating gravity serves as 80kgf(s). At this time, the exciting force with the desirable period of 25Hz is 150kgf(s). Therefore, exciting force-ed is $150 / 80 = 1.88$.

[0042] Although about 10 is sufficient as the upper limit of exciting force-ed when the processed member is made of the tough quality of the materials, such as a ferrous material, it is desirable to make the upper limit of exciting force-ed or less into five with the weak quality of the materials, such as a rare earth magnet, a bond magnet, ceramics, and glass. Moreover, as for especially the minimum of exciting force-ed, it is [one or more] desirable that it is 1.5 or more. If exciting force-ed is smaller than this minimum, a coat growth rate will become slow, on the other hand, when larger [than an upper limit] and a processed member is the weak quality of the material, that destruction becomes easy to take place, and deformation of a coat formation medium also becomes easy to take place. Although especially the frequency of vibration is not limited, it is desirable that it is the range of 2Hz - 200Hz. The amplitude at this time goes into the range of the above-mentioned exciting force-ed by 0.5-10mm.

[0043] Then, in the case of a churning method, it is desirable for the centrifugal force generated by rotation to

be contained in the range of the above-mentioned exciting force-ed to the sum total weight of coat formation mixture and a container. However, if a rotational frequency is too large and the volume rate of the coat formation mixture in/or a container is too large, coat formation mixture will be pushed against a vessel wall, and mixing will not fully take place. Therefore, as for 60 or less rpm and/, or the aforementioned volume rate, it is [a rotational frequency] desirable to fulfill 80% or less of conditions.

[0044] The equipment furthermore shown in drawing 8 as an excitation method can be used. Vibration exciter 8 is attached in the inferior surface of tongue of 20, and it is with the shape of U character which attached the 1-20-degree inclination preferably, and is as while adding vibration to the coat formation mixture 10, and 20 tops are slid down. A cross-section configuration is not limited to U typeface, but can use the thing of various configurations, such as circular, V typeface, and a square shape. Moreover, the upper part of a flume 20 does not necessarily need to be released. The vibrating screen 22 is installed down the lower limit of a flume 20. The vibrating screen 22 is smaller than the processed member 23, fixes a larger mesh than the coat formation media 24, such as a steel ball, to a frame etc., and it connects it with vibration exciter while making the whole incline. Therefore, the coat formation mixture which fell on the vibrating screen 22 passes through a mesh with the coat formation medium 24, and falls caudad, and, on the other hand, the processed member 23 is conveyed on the vibrating screen 22. The coat formation medium 24 is recovered by the medium recovery conveyor 30 which the vibrating screen 22 formed caudad, and a reuse is carried out to coat formation use. Moreover, the processed member 23 is recovered by the recall conveyor 31 formed in the bottom edge of the vibrating screen 22. If the above equipments are used, continuation full automatic-ization of coat formation will be attained. Furthermore, a flume 20 can be made into the shape of a ** face crease or a whorl as shown in drawing 7, and occupancy area of a flume 20 can be lessened. If it is with this ** face crease and outlet 20a of 20 is brought just under insertion section 20 of coat formation mixture 20b b, the return path when carrying out the return of the coat formation medium can be shortened. Moreover, although illustration has not been carried out, it can hold a flume in a container and can also vibrate it the whole container.

[0045] It is desirable to mix a coat formation medium by vibration or stirring within a container, and to insert a processed member, the fine-particles matter, and resin in a container while mixing these media as insertion sequence to the container of each component of coat formation mixture, at serial or coincidence (the approach of claim 2). According to this approach, homogeneity mixing extent is raised. Although a coat formation medium is beforehand invested into a container here, and adhesion of resin required for coat formation is brought about by what vibration or stirring is added for and striking power can be generated, other processed members, the fine-particles matter and the insertion sequence of resin, a count, the independent charge, the coincidence charge, etc. is completely arbitrary. If the resin which contains a pigment as the approach of the coincidence charge is inserted in, the fine-particles matter and resin will become a container with the coincidence charge.

[0046] However, special insertion sequence may be desirable. ** When the resin melted into a solvent and resin fine particles (fine-particles matter) are used for liquefied resin or a solvent pan : beforehand, if only these and resin fine particles are mixed, in being easy to dissolve resin fine particles in liquefied resin, powdered condensation will tend to take place, and a uniform coat will not be obtained. Therefore, when powdered resin is inserted in a container at a late process or it inserts in a container previously, the liquefied resin inserted in later is inserted in a processed member and coincidence. ** When either of the components of coat formation mixture is heated : insert in resin after inserting in a container the processed member and the heated coat formation medium which inserts in the processed member which inserted in; resin which inserts in resin after heating a processed member and inserting in a container, and which carried out afterbaking and of which; heating was done.

[0047] By stiffening resin during vibration or stirring, the fixed force of the fine-particles matter caught by the resin coat can be heightened (the approach of claim 3). The approach of making it harden by the radiation irradiation of ultraviolet rays, a gamma ray, an electron ray, or others further etc. stiffened with a curing agent as the approach of hardening of resin using a 2 liquid hybrid model room-temperature-setting type of stiffening heat hardening mold resin with heating and of evaporating a solvent is possible.

[0048] Furthermore, coat formation mixture other than the fine-particles matter can be beforehand mixed within a container, and the fine-particles matter can be inserted in in a container afterwards (the approach of claim 4). The advantage by this approach is as following ** - **.

[0049] ** By spreading equally enough over a processed member front face resin with a large fluidity which was diluted especially with the solvent, a resin coat equal enough can be made and it can cover with the fine-particles matter to homogeneity.

[0050] ** As for the coat near the interface with the processed member used as a substrate, resin is set to rich, as for the front face of a coat, the fine-particles matter is set to rich, and the transition layer where the rate of these components changes continuously exists within a coat. Therefore, the adhesion force of a coat is high.

[0051] ** Near the front face of a coat, the fine-particles matter is pressed fit, and depending on the 70 - 90 volume % case, the rate of the fine-particles matter is almost very as high as 100%, and exceeds far the rate of pigment combination of a resin paint film. therefore, TiO_2 for which the fine-particles matter is used as a pigment of a coating, MgO , and Fe_2O_3 etc. -- it is -- as for a case, the engine performance for which a covering front face intercepts water and other corrosion components becomes very good. Usually, although the multilayer coating of the paint film is carried out and the amount of a pigment is made [many] in resin paint for heavy corrosion prevention, this requires time and effort, and in interlaminar peeling, it becomes empty and it has a lifting and the problem to which thickness becomes large. By this invention method, a coat with many pigments can be obtained by one processing, and there is an advantage that thickness is thin.

[0052] You form the resin coat in the processed member beforehand, and a processed member, a coat formation medium, and the fine-particles matter can make it vibrate or stir after that in this invention. Therefore, the exception method of this this invention is set to the approach of forming a coat in a processed member front face. The processed member which gave the first resin coat like a coat formation fault which is in the condition of not hardening, partially in the first stage at least, The fine-particles matter (it sets like a coat formation fault and there is a thing of hard resin powder rather than said resin), And it is the coat formation approach which a dimension is substantially larger than said processed member from said fine-particles matter, and is characterized by a dimension adding vibration or stirring to a small coat formation medium within a container substantially (claim 5).

[0053] This resin coat acts like the resin coat made to adhere to a processed member from the exterior in claim 1, and catches the fine-particles matter. Case [whose processed member is / like a resin bond magnet or a plastics member], if it is immersed in a solvent and this is pulled up, the resin near a magnetic front face begins to melt, and a resin coat can be made easily.

[0054] Furthermore, in case the exception method of this invention is enforced, the fine-particles matter can be sprinkled on a resin coat (that is, the fine-particles matter is pasted up using the adhesion force which the resin coat has), and the method according to account of the Gokami can be enforced.

[0055] In case the exception method of this invention is enforced, said resin (first resin) and congener, or resin (the second resin) of a different kind can be added into coat formation mixture (the approach of claim 6). The second resin flows on the resin coat already formed, makes a layer, grows and brings about association between fine-particles matter-resin. The resin mentioned above about claim 2 as this second resin can be used.

[0056] After mixing in this invention, by hardening the resin of the coat of the processed member in which the coat was formed, a coat can be made to be able to strengthen and adhesion can be improved again (the approach of claim 7). Hardening is left in the ordinary temperature which is in a mixed container or heats a coat to the polymerization temperature of resin out of a container, and is performed by evaporating a solvent etc. This hardening processing is effective, also when forming the coat of this invention on it further by making into a substrate the coat formed when a film strength, adhesion, etc. were inadequate and obtaining a multilayer coat. Furthermore depending on the class of resin, it can also harden with ultraviolet rays or a gamma ray, an electron ray, etc.

[0057] Immediately after coat formation, a lot of fine particles which are not fixed to a it top may remain, and when using the member processed by this invention by electrical and electric equipment, electronic parts, or a precision machinery component etc. which dislikes dust and dust, it is necessary to remove these fine particles. Therefore, it is desirable to remove isolation fine particles by approaches, such as ultrasonic cleaning and blasting of air, (the approach of claim 8). As for the hardening front stirrup of resin, next either can carry out removal of isolation fine particles.

[0058] It is also possible to rub a coat front face by the elastic medium in removal of isolation fine particles (the approach of claim 9). The elasticity medium and member which for that mix within a container the member in which an elastic medium and an elastic coat were formed, for example, add vibration to a container can be

agitated. By this approach, according to the shearing force between an elastic medium and residual powder, residual powder is removed and, in addition, the front face of a coat is polished. As for this approach, an appearance with it is acquired. [the large and removal effectiveness of residual powder and] [more beautiful than ultrasonic cleaning] Therefore, it is suitable when using the member of this invention for an ornament supply and a sheathing supply.

[0059] As the above-mentioned elastic medium, since itself has impact absorptive power to some extent, what does not damage the coat which gave striking power strong against a processed member, and was formed, or is not shaved off deeply is desirable. For example, saw dust, wood powder, walnut husks, flexible plastics, rubber, etc. are desirable. Furthermore oil etc. can be infiltrated into saw dust etc. and the effectiveness or rust-proofing nature of surface polishing can also be raised.

[0060] Moreover, it can heat-treat to the processed member after the coat formation concerning this invention (the approach of claim 10). As for this purpose, one is hardening of resin. Although the curing temperature of resin changes with classes of resin, generally it is 30-200 degrees C, and the setting time is about 1 - 500 minutes. Resin can be stiffened by performing heat treatment of this temperature and time amount.

[0061] Other purposes of heat treatment are increasing the particles of the fine-particles matter, or the bonding strength between the fine-particles matter and a processed member by thermal diffusion. It is considering as the film which the pinhole of a coat was furthermore decreased and continued as much as possible. Moreover, homogenization of the membranous quality by diffusion between each class of multilayers and improvement in corrosion resistance or a mechanical property may be meant.

[0062] More than $M_p (1/3)$ of the temperature of heat treatment is desirable at below the melting point ($M_p:K$) of the fine-particles matter. if heat treatment temperature exceeds the melting point of the fine-particles matter - the fine-particles matter -- melting -- a molten bath -- joining of who or members is started. The target effectiveness will be hard to be acquired if heat treatment temperature is lower than one third of the melting points. Since this heat treatment temperature must naturally be lower than the melting point of a processed member, this approach is applied to the processed member which consists of matter with the melting point higher than heat treatment temperature. Moreover, since heat treatment temperature becomes usually higher than the decomposition temperature of resin, most coats consist of fine-particles matter after heat treatment. When applying this approach, the thing which decomposition evaporation is easily carried out [thing] comparatively at low temperature, and does not make carbon etc. remain to a coat, for example, paraffin, polypropylene, various waxes of resin, etc. are desirable. Moreover, resin is before heat treatment and it is desirable for there to be as much as possible few content rates in a coat. The percentage is 50% or less.

[0063] The above-mentioned heat treatment is effective when the fine-particles matter is a low-melt point point comparatively like Zn, Sn, or these alloys. That is, although these Zn etc. can carry out the corrosion prevention of almost all the metals according to the sacrifice corrosion prevention effectiveness, it is required for coat structure to be close to the continuation film for that purpose. Although the sacrifice corrosion prevention effectiveness is not fully demonstrated in severe corrosive environment which is continuously exposed to storm sewage and salt water in the coat which the fine-particles matter obtained by this invention approach distributed, the sacrifice corrosion prevention effectiveness which gives corrosion resistance good enough is acquired by heat treatment. Although the coat of Zn and Sn had been conventionally formed of electroplating or hot dipping, since the former was a wet process, it had waste water and the problem of by-product processing, plating thickness was as thick as 100 micrometers or more, and a thin coat was not obtained, but the latter had the problem of not being suitable in the bit and piece again. On the other hand, since this invention method can form a thin coat in a bit and piece according to a simple dry process, it is suitable for the field of the corrosion-resistant coat formation accompanied by a problem by electroplating or hot dipping.

[0064] Furthermore, although it can heat-treat in atmospheric air when the fine-particles matter is matter with high corrosion resistance, such as aluminum and Sn, it is desirable to heat-treat in a vacuum or inert gas.

[0065] Then, the approach of claim 11 is an approach of giving the protective film of resin to the front face of the above-mentioned coat. This approach is effective in raising the reinforcement of a coat, and corrosion resistance, when applied to the coat which does not heat-treat. Even if there are few pitches and they remove residual fine particles, the powdered fixed force of the front face of a coat is in addition weak. Since this invention member does not have the intention of the use as a slide member, the force is not continuously applied to a coat from the exterior, but when under handling and a member are attached in a machine and

impulse force and the strong force are applied from the exterior to inside, the fine-particles matter may be omitted or a coat may be destroyed locally. In order to prevent such un-arranging, it is effective to give the coat of resin. The coat of resin smooths a front face, and a fine sight also raises it, it fills a pinhole further, and bars osmosis of moisture.

[0066] If resin covering is applied to the coat which heat-treated, high heat treatment temperature cannot be taken, but this will be sealed and closed, when full removal of a pinhole etc. is difficult, or when air bubbles and a crack arise during heat treatment.

[0067] Although a spray or a processed member may be made immersed into resin, the approach of resin covering formation can form a coat in homogeneity thinly, if a resin coat formation medium is used like an approach according to claim 12. A resin coat formation medium applies the principle of the first coat formation medium of this invention to resin covering formation.

[0068] Furthermore, paint of the usual coating containing a pigment can also perform resin covering (approach according to claim 13). In this case, in addition to the effectiveness of resin covering mentioned above, a good fine sight can be obtained.

[0069] Moreover, as a protective film, the plating of a metal or an alloy or the distributed plating (electroplating or electrolysis plating) of a metal and a nonmetal other than a resin coat can be performed (the approach of claim 14). It was difficult to perform electroplating directly as substrates are non-conductive matter, such as ceramics and plastics, conventionally or conductivity is the bad uneven matter like a resin bond magnet, and complicated pretreatment was required though it was possible. Therefore, after carrying out nonelectrolytic plating to the substrate, generally the cost which performs electroplating, and the method of taking time and effort were performed. on the other hand, this invention -- a substrate -- a metal -- since a rich layer can be given firmly and easily, electroplating of the non-conductive matter becomes very easy.

[0070] Moreover, even if it was the matter which can be galvanized conventionally, it was difficult to adjust the presentation of plating alloy metallurgy group-nonmetal composite coatings in the large range. On the other hand, since this invention forms a coat with a non-electrochemical process, its range of presentation accommodation is very wide.

[0071] Moreover, conventionally, by the chemical reaction of the plating electrolytic solution and a processed member, plating is difficult or there was a case of being impossible. This invention makes plating possible easily, also when starting. There is plating to a powder metallurgy ingredient as the example. Since this has pore, if it makes the plating electrolytic solution contact, plating liquid will permeate even the interior and electrodeposition will take place to internal corrosion or the interior of un-wanting. Although what is necessary is to have formed the metallic film upwards by PVD etc. and just to galvanize, in order to avoid this, PVD needs large-scale equipment. On the other hand, according to this invention method, the substrate of plating can be made by the very easy approach. Although activity light metals, such as Ag and Mg, or those alloys were not able to be galvanized if the member to plating liquid melted, **** happened and they did not perform special pretreatments, such as zincate processing, according to this invention method, plating to such a member is also enabled by the easy approach.

[0072] Since, as for the fine-particles matter coat of this invention used as the substrate of a plating coat, some pinholes are formed in the gap of the particle of the fine-particles matter etc., a pinhole may be formed also in a plating coat. In this case, the pinhole in a plating coat can be prevented by thickening a plating coat a little or forming a nonelectrolytic plating coat in the substrate of a plating coat very thinly.

[0073] Claims 16 and 17 are related with a processed member with very advantageous application of the coat by this invention approach. Before explaining the advantage, the conventional technique is explained per a rare earth magnet and its protective film.

[0074] As for the outstanding magnetic properties, therefore need, the increment of a rare earth permanent magnet is being enhanced. Almost all the rare earth permanent magnets by which current production is carried out are the Sm-Co system which uses Sm and Co as a principal component, and a Nd-Fe-B system, and the resin bond magnet combined with what depended on sintering as a manufacturing method, and resin is almost the case. After a resin bond magnet presses the approach of performing compression molding after mixing resin with magnet powder, and hardening resin after that, an injection-molding method, and magnet powder, it is manufactured by the approach of infiltrating resin etc. since the rare earth magnet contains activity rare earth elements so much -- an elevated temperature -- if used in a humid environment, dispersion in the performance

degradation by corrosion or the engine performance will be produced, and the quality of a corrosion product will serve as a pollution source. In order that especially a Nd-Fe-B magnet may use iron as a principal component, corrosion resistance is low, grant of a protective coating is indispensable, and spraying and electropainting, such as an epoxy resin, are performed [as opposed to / in current and nickel plating / sintering and a resin bond magnet] as opposed to the sintered magnet. However, nickel plating performed to a Nd-Fe-B sintered magnet with many bits and pieces also has the problem that problems, such as trouble and waste fluid processing, have plating actuation as the galvanizing method was already explained, and also the adhesion of the plating by removal of the oxide of a substrate being inadequate is inferior. There are problems, like as paint of resin was also already explained, paint actuation takes time and effort.

[0075] Moreover, since a bond magnet has the cheap price, and multilayer paint of resin is not realistic, monolayer paint is in use. For this reason, the corrosion resistance of a resin bond magnet has stopped at level lower than a sintered magnet. as a cure of this fault dissolution, giving electroplating on a nonelectrolytic plating substrate is proposed -- **** (JP,3-116703,A) -- there is a problem which was mentioned above. If electropainting is used, corrosion resistance will improve a little from spray painting, but this also needs large-scale paint and a waste fluid processing facility, and in order to carry out by hanging to a fixture fundamentally, it serves as cost quantity. Furthermore, since a resin bond magnet is porosity much more, if it does not thicken nonelectrolytic plating fairly, it does not serve as a good substrate from a sintered product. Moreover, it is said that management of a bath presentation is very difficult for the nonelectrolytic plating liquid which uses a Nd-Fe-B system as a processed member.

[0076] The fine-particles-pitch powder coat formed in a rare earth magnet front face of this invention has the following advantages.

** In the case of a sintered magnet :: coat formation conditions that surface treatment is not needed [as opposed to / especially / the conventional plating coat] are loose (that is, it is not necessary to set up conditions especially bearing a Nd-Fe-B magnet in mind). the conventional resin coat -- receiving -- the stable oxide 2, for example, TiO₂, MgO, and Fe₂O₃ etc. -- corrosion resistance can be made good by distributing fine particles in a coat and making [many] the content especially on a coat front face.

[0077] It is TiO₂ to drawing 12 . The result of having investigated the cross-section structure of the coat obtained by the approach of three in the example 1 which used fine particles and an epoxy resin with the electron microscope photograph (one 10000 times the scale factor [a SEM image,] of this) is shown. what is visible in the shape of a particle by the whole coat among drawing -- TiO₂ it is . An epoxy resin appears in the shape of a continuous phase in the upper part of a coat, the lower parts, and these middle. Moreover, the particle with the indistinct profile which is visible to the lower left side of a coat is resin and TiO₂. Mixing is shown. TiO₂ Although the resin which intervenes between particles is clearly accepted by (), it is not clear with a photograph. The coats made by this invention approach have gathered very densely [fine particles] so that drawing 12 may show.

[0078] ** In the case of a resin bond magnet : since about the same corrosion resistance as multilayers is acquired to the conventional resin paint and the fine-particles matter and resin will be pressed fit in the hole of a resin bond magnet if a resin coat is first formed like [coat / conventional / monolayer resin]; whose corrosion resistance improves sharply, especially claims 6 and 7, a sealing effect is large, for this reason corrosion resistance improves. this invention coat which uses the conductive fine-particles matter to the conventional nonelectrolytic plating-electrolysis plating has very high industrial application possibility.

[0079] When a plating coat is formed on the fine-particles-pitch powder coat formed in the rare earth magnet front face of this invention, there are the following advantages.

** Since the plating substrate layer by this invention method has stuck firmly with resin on a base material front face in the case of a sintered magnet (comparing with the conventional plating coat), the plating coat which was excellent in adhesion is obtained by choosing a plating substrate layer appropriately to the plating layer formed on it. Moreover, although the plating coat usually had some pinhole, since the direct base material front face is arrived at as these pinholes are the conventional plating coats, the corrosion component which invaded from the pinhole permeates the interface on a plating layer and the front face of a base material, and tended to cause film peeling etc. When the oxidizing zone remains especially on the base material front face, they are a lifting and a cone about film peeling very much. However, by this invention method, since most corrosion components from a pinhole are altogether stopped by this substrate layer since the good resin of anti-corrosiveness and a powder-

mixing coat exist under a plating coat, and it is not spread on a base material front face, film peeling is lost. [0080] ** In the case of a resin bond magnet (comparing with the conventional nonelectrolytic plating) : generally the bath of nonelectrolytic plating is expensive, and since a large amount of costs start waste fluid processing etc., it serves as cost quantity. Moreover, several steps of adhesion force with a substrate is inferior to a resin coat. Moreover, generally thick-film-ization has limited nonelectrolytic plating to the thin film 5 micrometers or less difficultly, and since especially a bond magnet is a porous body, it gathers the pinhole on the front face of a base material, and serves as a very porous coat. Such film does not almost have the cutoff capacity of the corrosion component which permeates from the pinhole of the electrolysis plating film formed on it, and tends to produce dispersion, such as film peeling. Moreover, the plating liquid of nonelectrolytic plating tends to remain at the pinhole of a bond magnet, and becomes the cause of film peeling that this is also big. Nd system bond magnet which gave nonelectrolytic plating has not yet resulted in mass production for these troubles.

[0081] According to this invention method, the closure of the pinhole on the front face of a magnet is carried out with resin, and since it is firmly stuck to the metal layer which serves as a substrate of plating by this resin layer further, the plating coat formed on it also has good adhesion. In order that this substrate layer may prevent diffusion of the corrosion component on the front face of a magnet like **, the corrosion resistance excellent farther as a result than a conventional method is acquired.

[0082] Although how to form a coat with resin was explained by the approach explained above, the silicate represented by the adhesion matter of an inorganic system, for example, water glass, can form a glass coat in a processed member front face by being able to make it distribute the fine-particles matter, a coat formation medium, and a processed member uniformly and mix, and making it fall by temperature, the solvent, or water dilution, while mixing viscosity. Moreover, a glass coat can catch the fine-particles matter. Therefore, it can replace with resin or the inorganic adhesion matter can be used with resin.

[0083] Hereafter, an example explains this invention in detail.

[Example]

Example 1 Fe81Nd13 B6 The powder for quenching bond magnets with a grain size [with a presentation] of 100 micrometers or less was used. this powder -- an epoxy resin -- 3wt(s)% -- in addition, it mixed, it pressed with the welding pressure of 5 ton/cm², and 220 22mm phix20mm phix10mm Plastic solids were acquired. This for 1 hour, and it considered as the resin bond magnet. [150 degrees C] Next, having carried out 10kg (apparent density of 5kg/l.) injection of the diameter phi3.0mm shot, and adding vibration with a vibration frequency 2500c.p.m. (cycle per minute) and an amplitude of 5mm to a circular pot with a volume [of 2.8l.], and a depth of 150mm, 20g of aluminum powder with an average grain size of 1 micrometer was thrown in, and vibration was added to aluminum powder for 5 minutes.

[0084] Next, 20 magnets which were immersed in the methyl ethyl ketone (MEK) which melted 10% (97% of resin, 3% of curing agents) of epoxy resins beforehand, and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. Carried out 2hr heating at 120 degrees C, finally put into the pot of the same size with 2.0kg of walnut shell pieces with a mean particle diameter of 2mm, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed. The conditions of RH estimated corrosion resistance for the magnet which formed the coat of 10 micrometers of average thickness (maximum of 5 micrometers, minimum value of 2 micrometers) by the above approach 85 degree-Cx90%. The result is shown in Table 1 as "1."

[0085] the same approach as the following -- however, it created at a time 20 magnets (2-11) which changed the following conditions and covered powder, respectively.

It replaced with 2-aluminum powder and Cu powder whose mean particle diameter is 1 micrometer was used. TiO₂ whose mean particle diameter it replaces with 3-aluminum powder and is 0.3 micrometers Powder was used.

aluminum 2O₃ whose mean particle diameter it replaces with 4-aluminum powder and is 1 micrometer Powder was used.

It replaced with 5-aluminum powder and the MgO powder whose mean particle diameter is 2 micrometers was used.

Fe 2O₃ whose mean particle diameter it replaces with 6-aluminum powder and is 2 micrometers Powder was used.

Fe 2O₃ whose mean particle diameter it replaces with 7-aluminum powder and is 2 micrometers Powder was used.

After replacing with 8-aluminum powder and forming the coat whose thickness is 5 micrometers using Cu powder whose mean particle diameter is 1 micrometer, nickel plating layer of 10-micrometer thickness was formed with electrolysis plating.

To 9-resin bond magnet, it is TiO₂. The addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of an average of 10-micrometer thickness (example of a comparison).

Spray blasting of the phosphoric-acid zinc chemical conversion liquid is carried out to 10-resin bond magnet, and it is after desiccation and TiO₂. The addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness (example of a comparison).

A coat was not given to 11-resin bond magnet, but it examined as it is (example of a comparison).

The 20-piece each humidity cabinet test of the resin bond magnet which formed various coats as mentioned above was carried out, and corrosion resistance was evaluated. Test condition: 85 degree-Cx90%RH neglect (check item: appearance)

A result is shown in degree table.

[0086]

[Table 1]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	B	C	D
2	A	B	B	C
3	A	A	B	B
4	A	A	B	C
5	A	A	B	B
6	A	A	B	B
7	A	A	A	B
8	A	A	A	A
9	B	C	E	—
10	A	B	D	—
11	D	E	—	—

Criterion A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole The whole rusting remarkable to 30% or more, a film blister, peeling [0087] Example 2SmCo_{4.8} Bond magnet powder with an average grain size [with a presentation] of 20 micrometers was used. this powder -- an epoxy resin -- 3wt(s)% -- adding -- mixing -- 5 t/cm² It pressed

with welding pressure and 80 22mm phix20mm phix10mm Plastic solids were acquired. This for 1 hour, and it considered as the resin bond magnet. [150 degrees C] Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 20g of aluminum powder with an average grain size of 1 micrometer was thrown in, and vibration was added to aluminum powder and a shot for 5 minutes. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. After carrying out 2hr heating of the magnet at 120 degrees C and carrying out the cure of the epoxy resin, finally, with 2kg of walnut husks with a mean particle diameter of 2mm, put into the pot of the same size as the object for coat formation, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed. [0088] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90% (check item-appearance). The result is shown in Table 2. The figure of front Naka and the left column means the following processings, respectively.

1 - TiO₂ whose mean particle diameter the coat whose average thickness is 10 micrometers is replaced with formation 2-aluminum powder by the above-mentioned processing, and is 0.3 micrometers Powder was used. To 3-resin bond magnet, it is TiO₂. The addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness (example of a comparison).

A coat was not given to 4-resin bond magnet, but it examined as it is (example of a comparison).

[0089]

[Table 2]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	B
2	A	A	A	A
3	A	A	B	B
4	C	C	D	E

Criterion A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole The whole rusting remarkable to 30% or more, a film blister, peeling [0090] Example 3Sm8.3 (Co0.72Fe0.2 Cu0.06Zr0.03) The powder for bond magnets with a grain size [with a presentation] of 100 micrometers or less was used. To this powder, 3wt(s)% is added, an epoxy resin is mixed, and it is 5 t/cm². It pressed with welding pressure and 100 22mm phix20mm phix10mm Plastic solids were acquired. This for 1 hour, and it considered as the resin bond magnet. [150 degrees C] Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 20g of Cu powder with an average grain size of 1 micrometer was thrown in, and vibration was added to Cu powder during 5 minutes, and a shot. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. Next, after carrying out 2hr heating of the magnet at 120 degrees C and carrying out the cure of the epoxy resin, put into the pot of the same size as the object for coat formation at the last with 2kg of walnut husks with a mean particle diameter of 2mm, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed. It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-

Cx90% (check item-appearance). The result is shown in Table 2.

[0091] The figure of front Naka and the left column means the following processings, respectively.

1 - The coat whose average thickness is 10 micrometers was replaced with formation 2-Cu powder by the above-mentioned processing, and the MgO powder whose mean particle diameter is 1 micrometer was used. Fe₂O₃ whose mean particle diameter it replaces with 3-Cu powder and is 1 micrometer Powder was used. To 4-resin bond magnet, it is TiO₂. The addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness (example of a comparison).

A coat was not given to 5-resin bond magnet, but it examined as it is (example of a comparison).

[0092]

[Table 3]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	B
2	A	A	A	A
3	A	A	A	A
4	A	A	B	B
5	B	C	C	D

Criterion A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole The whole rusting remarkable to 30% or more, a film blister, peeling [0093] Example 4Sm2 Fe17N3 The powder for bond magnets with an average grain size [with a presentation] of 2.5 micrometers was used. To this powder, 3wt(s)% is added, an epoxy resin is mixed, and it is 5 t/cm². It pressed with welding pressure and 80 22mm phix20mm phix10mm Plastic solids were acquired. This for 1 hour, and it considered as the resin bond magnet. [150 degrees C] Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 20g of aluminum powder with an average grain size of 1 micrometer was thrown in, and vibration was added to aluminum powder and a shot for 5 minutes. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. After carrying out 2hr heating of the magnet at 120 degrees C and carrying out the cure of the epoxy resin, put into the pot of the same size as the object for coat formation at the last with 0.2kg of walnut husks with a mean particle diameter of 2mm, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0094] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90% (check item-appearance). The result is shown in Table 4.

[0095] The figure of front Naka and the left column means the following processings, respectively.

1 - TiO₂ whose mean particle diameter the coat whose average thickness is 10 micrometers is replaced with formation 2-aluminum powder by the above-mentioned processing, and is 0.3 micrometers Powder was used. To 3-resin bond magnet, it is TiO₂. The addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness (example of a comparison).

A coat was not given to 4-resin bond magnet, but it examined as it is (example of a comparison).

[0096]

[Table 4]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	B	C
2	A	A	B	B
3	B	B	C	E
4	D	D	E	—

A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole The whole rusting remarkable to 30% or more, a film blister, peeling [0097] Example 5Nd13.8Dy0.4 Fe 78.2B7.6 Coarse grinding of the ingot with a presentation was carried out so that a mean diameter might be set to 20 micrometers with a stamp mill, and it ground so that a mean diameter might next be set to 3.0 micrometers with a jet mill. They are 1.5 t/cm² to a magnetic field and the direction of a right angle in metal mold, applying the magnetic field of 12kOe(s) to this pulverizing powder. It pressurized by the force and the green compact was obtained. After sintering this green compact at 1100 degrees C in a vacuum for 2 hours, aging treatment was carried out at 650 degrees C for 1 hour, and 120 sintered compacts were obtained. After grinding this sintered compact completely by the grinder, centrifugal barrel finishing dropped the corner and washing desiccation was carried out continuously. The dimension of a product was 20mm phix5mm discoid. Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 20g of aluminum powder with an average grain size of 1 micrometer was thrown in, and vibration was added to aluminum powder and a shot for 5 minutes. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. After carrying out 2hr heating of the resin at 120 degrees C and carrying out the cure of the epoxy resin, put into the pot of the size same [2kg of walnut husks with a mean particle diameter of 2mm] as the last, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0098] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90%. The result is shown in Table 5.

[0099] The figure of front Naka and the left column means the following processings, respectively.

1 - TiO₂ whose mean particle diameter the coat whose average thickness is 10 micrometers is replaced with formation 2-aluminum powder by the above-mentioned processing, and is 0.3 micrometers Powder was used. TiO₂ whose mean particle diameter it replaces with 3-aluminum powder and is 0.3 micrometers TiO₂ whose mean particle diameter it is immersed in an epoxy resin (5%MEK solution), and is 0.3 micrometers again after forming a coat using powder (residual powder not removing) The coat was formed using powder (residual powder not removing). Then, residual powder with walnut husks was continuously carried out [for 2 hours] the cure and removed at 120 degrees C, and average thickness formed the 20 micrometers (maximum of 27 micrometers, minimum value of 18 micrometers) coat.

TiO₂ whose mean particle diameter it replaces with 4-aluminum powder and is 1 micrometer TiO₂ whose mean particle diameter it is immersed in an epoxy resin (5%MEK solution), and is 0.3 micrometers again after forming a coat using powder (residual powder not removing) The coat was formed using powder (residual powder not removing). The epoxy resin (5%MEK solution) was immersed and followed further after that, residual powder with walnut husks was continuously carried out [for 2 hours] the cure and removed at 120

degrees C, and average thickness formed the 22 micrometers (maximum of 29 micrometers, minimum value of 20 micrometers) coat.

Fe 2O₃ whose mean particle diameter it replaces with 5-aluminum powder and is 1 micrometer Powder was used.

To 6-resin bond magnet, it is TiO₂. The addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness (example of a comparison).

A coat was not given to 7-resin bond magnet, but it examined as it is (example of a comparison).

[0100]

[Table 5]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	B	B	C
2	A	A	B	C
3	A	A	A	B
4	A	A	A	A
5	A	A	B	B
6	C	E	—	—
7	E	—	—	—

Criterion A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole The whole rusting remarkable to 30% or more, a film blister, peeling [0101] Example 6SmCo_{4.6} Coarse grinding of the ingot with a presentation was carried out so that a mean diameter might be set to 25 micrometers with a stamp mill, and it ground so that a mean diameter might next be set to 4.0 micrometers with a jet mill. They are 1.5 t/cm² to a magnetic field and the direction of a right angle in metal mold, applying the magnetic field of 12kOe(s) to this pulverizing powder. It pressurized by the force and the green compact was obtained. This green compact was sintered at 1210 degrees C in the vacuum for 2 hours, it cooled slowly after that, and 80 sintered compacts were obtained. After grinding this sintered compact completely by the grinder, centrifugal barrel finishing dropped the corner and washing desiccation was carried out. The dimension of a product was 20mm phi x 5mm discoid. Next, it is TiO₂ with an average grain size of 0.3 micrometers, feeding 10kg of diameter phi 3.0mm shots into a with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it. 20g of powder is thrown in and it is for [TiO₂] 5 minutes. Vibration was added to the shot. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. Put into the pot of the size same [2kg of walnut husks with a mean particle diameter of 2mm] as the last after 2hr heating at 120 degrees C, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0102] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-C x 90%. The result is shown in Table 6.

[0103] The figure of front Naka and the left column means the following processings, respectively.

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejje

12/5/2005

1 - It is formation 2 about the coat whose average thickness is 10 micrometers by the above-mentioned processing. - It is the coat whose average thickness the above-mentioned processing is performed twice and is 20 micrometers to a formation 3-sintered magnet TiO₂. The addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of an average of 20-micrometer thickness (example of a comparison).

A coat was not given to 4-sintered magnet but it examined as it is (example of a comparison).

[0104]

[Table 6]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	B
2	A	A	A	A
3	A	A	B	B
4	B	C	D	D

Criterion A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole The whole rusting remarkable to 30% or more, a film blister, peeling [0105] Example 7Sm7.3 (Co_{0.69}Fe_{0.2} Cu_{0.06}Zr_{0.03}) Coarse grinding of the ingot with a presentation was carried out so that a mean diameter might be set to 25 micrometers with a stamp mill, and it ground so that a mean diameter might next be set to 4.0 micrometers with a jet mill. They are 1.5 t/cm² to a magnetic field and the direction of a right angle in metal mold, applying the magnetic field of 12kOe(s) to this pulverizing powder. It pressurized by the force and the green compact was obtained. This green compact was sintered at 1215 degrees C in the vacuum for 2 hours, solution-ization was performed at 1170 degrees C for 1 hour, it cooled slowly after 2hr aging at 850 degrees C, and 80 sintered compacts were obtained. After grinding this sintered compact completely by the grinder, centrifugal barrel finishing dropped the corner and washing desiccation was carried out. The dimension of a product was 20mm phi x 5mm discoid. Next, it is TiO₂ with an average grain size of 0.3 micrometers, feeding 10kg of diameter phi 3.0mm shots into a with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 1500c.p.m. and an amplitude of 5mm to it. Powder is thrown in and it is for [TiO₂] 5 minutes. Vibration was added to powder and a shot. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. After carrying out 2hr heating of the magnet at 120 degrees C and hardening an epoxy resin, put into the pot of the size same [2kg of walnut husks with a mean particle diameter of 2mm] as the last, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0106] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90%. The result is shown in Table 7.

[0107] The figure of front Naka and the left column means the following processings, respectively.

1 - It is formation 2-TiO₂ about the coat whose average thickness is 10 micrometers by the above-mentioned processing. Fe₂O₃ whose mean particle diameter it replaces with powder and is 1 micrometer Powder was used.

3-TiO₂ It replaced with powder and aluminum powder whose mean particle diameter is 1 micrometer was used.

To 4-sintered magnet, it is TiO₂. The addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of an average of 20-

micrometer thickness (example of a comparison).

A coat was not given to 5-sintered magnet but it examined as it is (example of a comparison).

[0108]

[Table 7]

	2 5 0hr	5 0 0hr	1 0 0 0hr	1 5 0 0hr
1	A	A	A	A
2	A	A	A	A
3	A	A	B	B
4	A	A	B	B
5	B	C	D	D

Criterion A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole The whole rusting remarkable to 30% or more, a film blister, peeling [0109] The powder of the example 8 following was fabricated by the die pressing method, and the 25mm phi x 20mm phi x 10mm ring-like green compact was created.

(A) aluminum-2.75wt%Li Gas atomization powder average grain size 20-micrometer welding pressure 2ton / cm² (B) Mg Gas atomization powder average grain size 20-micrometer welding pressure 2ton / cm² [0110] These green compacts were sintered at 600 degrees C in Ar ambient atmosphere for 6 hours. Each consistency of a sintered compact was 90% of true density. Every 20 following covering processings each were performed to the obtained sintered compact.

** Put 10kg (apparent density of 5kg/l.) of diameter phi 3.0mm shots into a circular pot with a volume [of 2.8l.], and a depth of 150mm, supply 20g, vibrate TiO₂ powder with an average grain size of 1 micrometer for 5 minutes, and it is TiO₂ to homogeneity. Powder was distributed. The conditions of vibration were 5mm in vibration frequency 2500c.p.m. and amplitude.

[0111] Next, the member covered by the resin film by being immersed in a sintered compact was beforehand supplied to the methyl ethyl ketone (MEK) which melted 10% (epoxy resin 97wt% and curing agent 3wt%) of pitches, and vibration was continued for 15 more minutes. After carrying out 2hr heating of this at 120 degrees C, the powder of the surplus which remained on the member front face was removed by supplying to said pot and pot of the same size with 2kg (average grain size of 2mm) (apparent density of 1kg/l.) of crushed walnut husks, and making it vibrate for 5 minutes on the same conditions. Thickness was an average of 10 micrometers.

[0112] About 5-micrometer Cu film was given by the same approach as **** (1 micrometer of diameters of Cu powder, 15g use). Then, an average of 10 micrometers (maximum of 14 micrometers, minimum value of 8 micrometers) nickel plating film was made to form with electrolysis plating.

[0113] ** In this example (aluminum-Li, Mg), since aluminum and Mg have the ionization tendency very larger than nickel, nickel plating cannot be performed directly. Then, a member is immersed in commercial Zn permutation solution which consists of a sodium hydroxide, a zinc oxide, and another Rochell salt and minute amount additive, electrolysis nickel plating processing by the Watts bath was carried out, and an average of 10-micrometer nickel plating film was made to form after performing Zn permutation processing (zincate processing) to a front face.

[0114] ** An average of 10-micrometer epoxy resin (carbon black 20% addition) coat was formed in the sintered compact by spray painting.

** To the sintered compact, did not form the coat and it was examined.

Each coat forming method was shown in Table 8 by Above A and B, and 1-5.

[0115]

[Table 8]

		2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
A	1	A	A	A	B
	2	A	A	A	A
	3	A	E	—	—
	4	B	D	E	—
	5	E	—	—	—
B	1	A	A	A	A
	2	A	A	A	A
	3	A	E	—	—
	4	B	D	E	—
	5	E	—	—	—

test condition: -- respectively -- 20 pieces -- 85 degree-Cx90%RH neglect check item: -- appearance criterion A *****-less all total B Macroscopically with no rusting. spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole the whole rusting remarkable to 30% or more, a film blister, and peeling rust -- face powder -- many film peeling considered that ** believed to be aluminum of a ** or the oxide of Mg is based on the residual of plating liquid was seen.

[0116] The powder of the example 9 following was fabricated by the die pressing method, and the 20mmx20mmx5mm plate-like green compact was created.

(A) Fe-0.3%C Electrolysis annealing powder (average grain size of 50 micrometers)

Welding pressure 3ton / cm² (B) aluminum-1%Si Gas atomization powder (average grain size of 25 micrometers)

Welding pressure 3ton / cm² In the vacuum, about (A), it sintered at 1300 degrees C, and sintered at 600 degrees C about (B) for 6 hours for 6 hours. The consistency of a sintered compact was [(A)] 90% about (B) 85%. Every 20 following covering processings each were performed to the obtained sintered compact.

** Put 10kg (apparent density of 5kg/l.) of diameter phi3.0mm shots into a circular pot with a volume [of 2.8l.], and a depth of 150mm, and it is Fe 2O₃ with an average grain size of 1 micrometer. 20g is supplied, powder is vibrated for 5 minutes, and it is Fe 2O₃ to homogeneity. Powder was distributed. The conditions of vibration were 5mm in vibration frequency 2500c.p.m. and amplitude.

[0117] Next, by being beforehand immersed in the methyl ethyl ketone (MEK) which melted 10% (epoxy resin 97wt% and curing agent 3wt%) of pitches, the member covered by the resin film was supplied and vibration was continued for 15 more minutes. After carrying out 2hr heating of this at 120 degrees C, the powder of the surplus which remained on the member front face was removed by supplying to said pot and pot of the same size with 2kg (average grain size of 2mm) (apparent density of 1kg/l.) of crushed walnut husks, and making it

vibrate for 5 minutes on the same conditions. Thickness was an average of 10 micrometers.

[0118] About 5-micrometer Cu film was given by the same approach as **** (1 micrometer of diameters of Cu powder, 15g use). Then, an average of 10-micrometer nickel plating film was made to form with electrolysis plating.

[0119] ** An average of 10-micrometer nickel plating film was made to form a member with electrolysis plating after Zn permutation processing like example 8-** beforehand.

[0120] ** Thickness made the epoxy resin coat (TiO₂ 20% addition) which is an average of 10 micrometers form by spray painting.

** Those without covering [0121] The neutral salt spray test (35 degrees C, 5%NaCl) by the JIS corrosion test approach was performed to the sintered compact which processed more than, and appearance observation was performed. A result is shown in Table 9. Each coat forming method was shown in Table 9 by Above A and B, and 1-5.

[0122]

[Table 9]

		2 4 hr	4 8 hr	1 2 0 hr	2 4 0 hr
A	1	A	A	C	C
	2	A	A	A	A
	3	C	D	E	—
	4	C	E	—	—
	5	E	—	—	—
B	1	A	A	B	C
	2	A	A	A	A
	3	C	D	E	—
	4	B	C	E	—
	5	E	—	—	—

Criterion A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole About **, many blisters produced the whole rusting remarkable to 30% or more, a film blister, and peeling A and B on the plating film.

[0123] Example 10 following nonmetal member A-B was created.

A. The following raw material was mixed, and powder compacting of the nickel-Zn ferrite sintered compact (it is 98% to consistency-true density) was carried out, it was sintered, and was obtained. NiO:Fe₂O₃:ZnO=20:50:30 (mole ratio). The sintered compact was cut and ground and 15mmx15mmx5mm Brock was obtained.

B. The following raw material was mixed, and powder compacting of the Sr ferrite sintered compact (it is 98% to consistency-true density) was carried out, it was sintered, and was obtained. SrCO₃:Fe₂O₃=1:5.9 (mole ratio). The sintered compact was cut and ground and the 15mm phix4mm cylinder was obtained.

[0124] The next coat processing was performed to these nonmetal members A and B.

** It is TiO₂ by the same processing as an example 8. The coat was formed. (Drawing 10 , A-**, B-**)

** Spray painting of the epoxy resin (TiO₂ 20% addition) was carried out. (Drawing 10 , A-**, B-**)

It cut after processing and the thickness part blanket-like voice on a nonmetal member was observed under the microscope. A result is shown in drawing 10 . From drawing, it attaches and it understands this invention method ** for the paint with them to be possible in the corner section. [the thin surroundings and] [more uniform than conventional method **]

[0125] Metal mold shaping of the plastics member of a hemispherical bowl mold with a diameter [example 11 / of 40mm] and a thickness of 2mm was carried out. 10kg of diameter phi3.0mm shots is put into a circular pot with a volume [of 2.8l.], and a depth of 150mm, 10g of Cu powder with an average grain size of 1 micrometer was thrown in, and it was vibrated for 5 minutes. Next, MEK was sprayed all over the member, the front face was made into adhesiveness, it invested in said pot, and vibration was continued for 15 minutes. After taking out the plastics member after that and carrying out 2hr heating at 50 degrees C, put into another pot of the same size with 2kg (particle size of 2mm) of crushed walnut husks, it was made to vibrate for 5 minutes, and the residual powder on the front face of a member was taken and removed.

[0126] About 4-micrometer Cu layer was able to be formed in the member front face by this, the resistance of the front face which was infinite before processing was able to decrease to 0.2 - 0.5 ohm/cm, and nickel plating was able to be easily performed using the usual Watts bath. Although the tape test was performed to the member after plating, exfoliation did not take place.

[0127] The following processing was performed to 100 glass pieces of the heart mold shown in example 12 drawing 11 .

** When the MEK solution was used as resin 5%, and also 5g of gold dust with a mean particle diameter of 1 micrometer was invested by the same processing as an example 8 and it was made to vibrate for 15 minutes, about 2-micrometer beautiful ***** was given. Exfoliation was not seen by the tape test.

[0128] ** About 10-micrometer Cu leather ** was given by throwing in 20g of Cu powder with a mean particle diameter of 1 micrometer, and making it vibrate by the same processing as an example 8 for 15 minutes.

Thereby, the surface electrical resistance of a member became 0.2 - 0.5 ohm/cm, and changed into the condition in which electroplating is possible enough. The glossy very beautiful front face was obtained by giving about 2-micrometer gilding with electrolysis plating succeedingly.

[0129] Example 13Nd13.8Dy0.4 Fe 78.2B7.6 They are 1.5 t/cm² to a magnetic field and the direction of a right angle in metal mold, applying the magnetic field of 12kOe(s) to pulverizing powder so that coarse grinding of the ingot with a presentation may be carried out so that a mean diameter may be set to 20 micrometers with a stamp mill, and then a mean diameter may be set to 3.0 micrometers with a jet mill. It pressurized by the force and the green compact was obtained. After sintering this green compact at 1100 degrees C in a vacuum for 2 hours, aging treatment was carried out at 650 degrees C for 1 hour, and 60 sintered compacts were obtained. Washing desiccation was carried out, after grinding this sintered compact completely by the grinder and centrifugal barrel finishing dropped the corner. The dimension of a product was 20mm phix5mm discoid. Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 30g of tin powder with an average grain size of 1 micrometer was thrown in, and vibration was added to tin powder and a shot for 5 minutes. Next, 20 magnets which were beforehand immersed in the paraffin MEK solution 5%, and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. Finally put into the pot of the same size with 2kg of walnut shell pieces with a mean particle diameter of 2mm, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0130] Next, the member was heated and taken out in the 4-hour vacuum at 300 degrees C, and the conditions of RH estimated corrosion resistance 85 degree-Cx90%. [0131] which shows the result in Table 10 The figure of the left column of a table means the following processings.

1 Tin Processing Article (Average Thickness 10 Micrometers)

2 Spray Painting (Epoxy Resin; 2 20% Addition of TiO(s))

Average thickness 10micrometer3 Those without processing [0132]

[Table 10]

	2 5 0hr	5 0 0hr	1 0 0 0hr	1 5 0 0hr
1	A	A	A	A
2	C	E	—	—
3	E	—	—	—

Test condition: 85 degree-Cx90%RH neglect Check item: Appearance criterion A *****-less all total B Macroscopically with no rusting. Spotted rust C of the whole microscope order of less than 10% Spotted rust D which less than 10% of the whole understands visually A little big rusting E to less than 30% 10% or more of the whole The whole rusting remarkable to 30% or more, a film blister, peeling [0133]

[Effect of the Invention] Since this invention can give the fine-particles coat excellent in corrosion resistance and adhesion to various members by the simple approach as explained above, the applicability of a fine-particles coat is expanded conventionally. Furthermore, the corrosion resistance which was excellent by applying this invention method to the processed material from which corrosion resistance conventionally sufficient by resin paint is not acquired can be acquired.

[Translation done.]

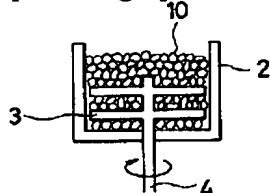
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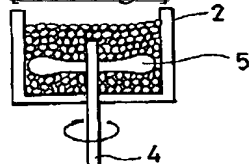
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DRAWINGS

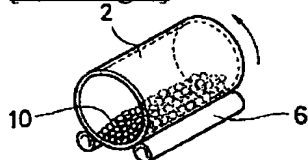
[Drawing 1]



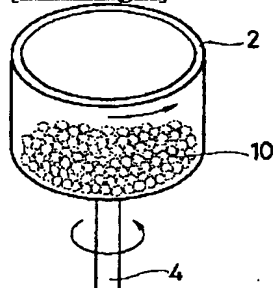
[Drawing 2]



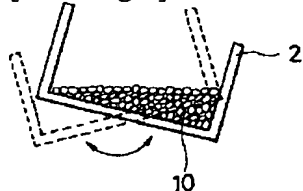
[Drawing 3]



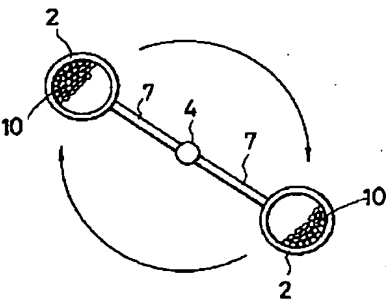
[Drawing 4]



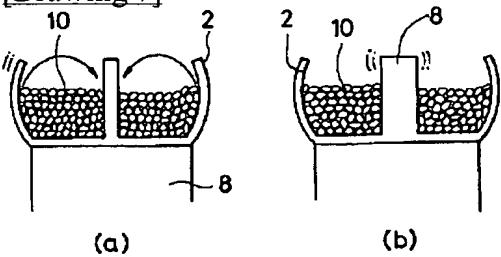
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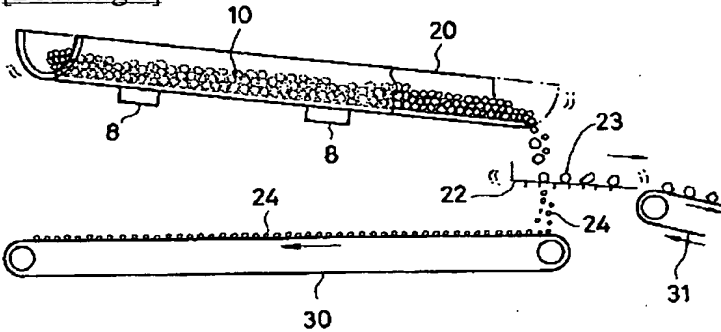
[Drawing 6]



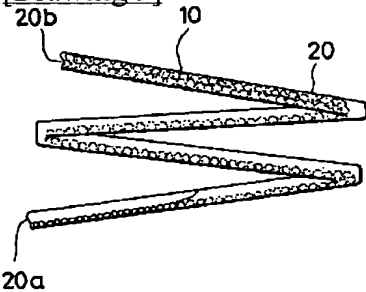
[Drawing 7]



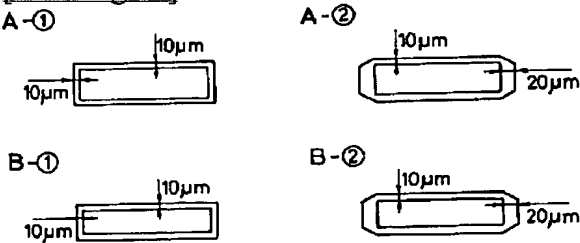
[Drawing 8]



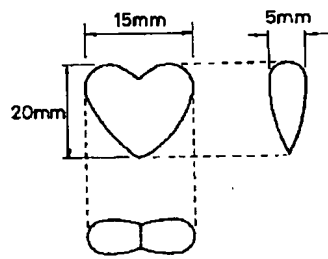
[Drawing 9]



[Drawing 10]



[Drawing 11]



[Drawing 12]



[Translation done.]

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CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law
 [Section partition] The 4th partition of the 3rd section
 [Publication date] May 25, Heisei 11 (1999)

[Publication No.] Publication number 5-302176
 [Date of Publication] November 16, Heisei 5 (1993)
 [Annual volume number] Open patent official report 5-3022
 [Application number] Japanese Patent Application No. 3-224782
 [International Patent Classification (6th Edition)]

C23C 26/00
 B05D 1/24

[FI]

C23C 26/00 Z
 B05D 1/24

[Procedure revision]
 [Filing Date] December 18, Heisei 9
 [Procedure amendment 1]
 [Document to be Amended] Specification
 [Item(s) to be Amended] Whole sentence
 [Method of Amendment] Modification
 [Proposed Amendment]
 [Document Name] Specification
 [Title of the Invention] The coat formation approach
 [Claim(s)]

[Claim 1] The coat formation approach characterized by forming the coat which contains the fine-particles matter in a processed member by applying striking power to a processed member by the coat formation medium while making the fine-particles matter adhere to the processed member by which the layer which has adhesion was formed at least in the part through a coat formation medium direct.

[Claim 2] The coat formation approach characterized by forming the coat which contains the fine-particles matter in a processed member by inserting in in a container the resin and the fine-particles matter for forming the layer which has adhesion in a processed member, a coat formation medium, and a processed member, and adding vibration or stirring to this container.

[Claim 3] The coat formation approach characterized by forming the coat which contains the fine-particles matter in a processed member by inserting it in the container with which vibration or stirring is added while the processed member by which the layer which has adhesion was formed at least in the part is inserted in a coat formation medium and the fine-particles matter.

[Claim 4] The coat formation approach characterized by forming the coat which contains the fine-particles matter in a processed member by inserting being simultaneous or serially the processed member and fine-

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww4.ipdl.ncipi.go... 12/5/2005

particles matter with which the layer which has adhesion was formed at least in the part in the container with which vibration or stirring is added while the coat formation medium is inserted in.

[Claim 5] The coat formation approach given in any 1 term of claims 1-4 characterized by hardening or removing the matter which constituted the layer which has the adhesion which remains in a coat after forming a coat in a processed member.

[Claim 6] The coat formation approach given in any 1 term of claims 1-4 characterized by removing the surplus fine-particles matter which remains on the front face of a coat after forming a coat in a processed member.

[Claim 7] The coat formation approach given in any 1 term of claims 1-6 characterized by heat-treating to the processed member in which the coat was formed.

[Claim 8] The coat formation approach given in any 1 term of claims 1-7 characterized by forming a coat in the processed member in which the coat was formed further.

[Claim 9] The coat formation approach according to claim 8 characterized by forming of paint the coat further formed in the processed member in which the coat was formed.

[Claim 10] The coat formation approach given in any 1 term of claims 1-7 characterized by forming the coat of a metal or an alloy in the processed member which formed the coat using the conductive fine-particles matter.

[Claim 11] The coat formation approach according to claim 10 characterized by forming the coat of a metal or an alloy with electroplating or nonelectrolytic plating.

[Claim 12] The coat formation approach given in any 1 term of claims 1-11 characterized by a processed member being a rare earth glow magnet.

[Claim 13] The coat formation approach given in any 1 term of claims 1-11 characterized by a processed member being a rare earth resin bond magnet.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the approach of forming a coat in the front face of various members. In addition, various well-known coats are already formed in the front face, or, as for various members, surface treatment may be given.

[0002] Moreover, the "coat" formed by the approach of the invention in this application aims at formation of the substrate layer for forming various, still better known coats for the purpose of corrosion prevention, mechanical-strength grant, the insulating stratification, and/or fine sight grant.

[0003]

[Description of the Prior Art] As a conventional technique which forms the coat of fine particles about amelioration of the approach of forming the coat of fine particles, the following approaches of this invention are well-known.

[0004] ** Powder coating

This approach is an approach of depositing powder coatings on the member which carried out preheating by spraying, spraying, ****, etc., they carrying out melting to it, and obtaining a paint film. Since this approach does not use a solvent, it does not have a public nuisance by the solvent, and has the advantage which is saving-resources-like. As patent reference about this approach, there are JP,2-258084,A, JP,57-13347,B, JP,53-29347,A, and JP,58-37029,B. Moreover, powder coating is performed by electrostatic spray painting.

[0005] ** Fine-particles coat

This approach is divided into that in which the processed member front face has adhesion, and the approach of being an adhesive property-ed. According to JP,2-71872,A belonging to the former, the fine-particles matter is contacted on the member front face which gave adhesiveness beforehand, the fine particles which added vibration to the member and adhered to the member front face are compressed below into bulk density, and the method of removing the powder which has not fixed to the posterior part material is indicated. As a member, the fluorescence toner is shown for the screen of color television in said official report as an example as fine particles.

[0006] JP,52-43731,A belonging to the latter puts in a metal or alloy powder, and the spherical or granular hard matter in metal goods in the air, rotates or vibrates these metal goods, and indicates the approach of covering a metal or alloy powder to a product inside. Fine particles are stuck to metal goods by pressure, and diffused junction is also performed by making diffusion cause between a powdered metal and the metal of a product with the heat energy which originates in vibration at coincidence. According to this approach, it is stated that the thermal resistance of the inside of a hollow product improves.

[0007] ** The metal powder rolling-out method

It is the approach of making metal powder adhere on the surface of a rolled plate, sticking powder to a rolled plate by pressure with roll rolling, and carrying out diffused junction by the postheat treatment (refer to JP,52-33840,A, No. 143531 [51 to], No. 54270 [57 to], and 47 No. -29232).

[0008]

[Problem(s) to be Solved by the Invention] The formation approach of a fine-particles coat has the following advantages to the various coat forming methods.

In order not to use :acid, alkali, etc. to electroplating or a nonelectrolytic plating method, while processing of processing waste fluid becomes unnecessary, even if a processed member is activity, problems, such as corrosion, do not arise.

Exposing :processed member to an elevated temperature to a hot-dipping method is avoided.

PVD and a CVD method -- receiving -- : -- large-scale equipment -- needlessness and productivity -- it is high.

[0009] However, it is required to satisfy the engine performance required of a coat for applying a fine-particles coat to various members, and also for the efficiency and dependability of the coat forming method to be high.

[0010] ** Since the metal powder rolling-out method is restricted to the quality of the material which a processed member is a plate and can be rolled out, a direct fine-particles coat cannot be formed in a machine part etc.

[0011] ** It cannot be said that it is efficient since the powder coating approach needs actuation of reversing or hanging it to ** etc. when processed members are accessories although it applies powder coatings to a processed member with spraying of a coating, a spray, etc. Moreover, there is a problem of being inapplicable in an ingredient with degradation of the quality of the material by heating a processed member etc.

[0012] ** Since powder was compressed by vibration between powder particles in the powder which is on it although it has a certain amount of [the fine particles in which the approach indicated by JP,2-71872,A among fine-particles coating adhered to the adhesive front face] adhesion force, when fine-particles covering requires external force, since there are also many dedropping and clearances where it becomes empty and a corrosive medium permeates easily, don't turn to the purposes, such as corrosion prevention. Furthermore, when a processed member has irregularity, the fine particles to a crevice are attached and the surroundings are poor.

[0013] ** The approach indicated by JP,52-43731,A among fine-particles coating performs mechanical association (sticking by pressure) and diffused junction to coincidence. For that, considerable energy is required, for example, the high-speed planetary mill of the vibration mill of 500kg of exciting force or rotation blow-hole RUU 300rpm is used in the example. Therefore, a processed member needs for reinforcement to be high and neither a ceramic nor the plastics with low reinforcement serves as a processed member. Moreover, since weak fine particles, such as an oxide, are destroyed by vibration, it is inapplicable.

[0014] The approach indicated by above-shown JP,52-43731,A is not employable as the approach of forming a coat in the various members which can apply only to covering of only an inside, and are said by this invention since considerable high energy is required. ** Although application to various members is possible for the approach of JP,2-71872,A among the powder coating approach and fine-particles coating of **, since there are the above problems, this invention aims at offering the coat formation approach which adhesion force is excellent in and can form a precise fine-particles coat while it raises the efficiency of fine-particles covering formation.

[0015]

[Means for Solving the Problem and its Function] In the fine-particles coat forming method in this invention method, the features-place is in below compared with a conventional method. If the adhesion matter, the fine-particles matter, and a processed member are vibrated or stirred within a container with a coat formation medium, the layer of the adhesion matter will be first formed in a processed member front face. Since contact of a member front face, the adhesion matter and a member front face, and a fine-particles particle takes place to coincidence when the thickness of this adhesion matter layer changes by the order of materials charging of the fine-particles matter, the adhesion matter, a coat formation medium, and a processed member, or the mixed method, for example, an injection of the adhesion matter and the fine-particles matter is performed to coincidence, it may become [whether the adhesion matter independent layer formed in a member front face becomes very thin, and] detection difficulty.

[0016] Adhesion matter coat formation is followed, and the fine-particles matter is caught and fixed by the adhesion matter layer according to the adhesion of an adhesion matter layer. Similarly, when an adhesion matter

layer hardens on a processed member front face, the fine-particles matter is caught and hardened. Since the coat formation medium which has received vibration or stirring is pressed fit between the particles which gave striking power to the fine-particles matter which has received vibration or stirring similarly, were caught by the adhesion matter layer and were already stuffed into it in the particle of said fine-particles matter, in addition to the adhesion of the adhesion matter etc., the fine-particles matter is fixed still more strongly by the striking power of a coat formation medium. Moreover, a collision of a processed member comrade also takes place in part, and press fit of the fine-particles matter is promoted similarly. Therefore, many fine-particles matter comes to be gradually mixed by the adhesion matter layer, and a coat continues growing.

[0017] Since association is made between the adhesion matter and the fine-particles matter and also the particle comrade of the fine-particles matter collides on a processed member front face through the striking power of a coat formation medium as explained above, the bonding strength by plastic deformation and the diffusion between atoms according to frictional heat secondarily is mainly made also among these. Especially when the fine-particles matter is the metal which is rich in ductility like aluminum, Cu, Zn, Sn, Au, Ag, Pb(s), and these alloys, an alloy, or plastics, these powder particle that collided deforms plastically and it is joined like a pressure welding. Moreover, such junction takes place also between the fine-particles matter and a processed member. As a result, the configuration of the matter in a coat becomes firm. The coat stratification according that the fine-particles matter is inductility matter to association between fine-particles particles and this stops being able to happen easily.

[0018] The coat formation medium which collides with a coat front face presses out the adhesion matter from between the particles of the fine-particles matter, and the adhesion matter oozes on the coat front face under formation. The adhesion matter adheres also to a coat formation medium in part. This adhesion matter adheres also to a processed member front face again, in case a coat formation medium collides with other processed member front faces. A fine-particles particle adheres to this resin layer front face. The extraction of such adhesion matter and the above-mentioned coat growth advance to coincidence. However, the rate of the fine-particles matter in a coat front face increases with membranous growth. then, a coat formation medium deals a blow to the fine-particles matter in a coat front face -- while coming out, and condensing the fine-particles matter and the rate of the adhesion matter decreasing increasingly, a growth-of-anodic-oxide-film rate falls. This is because the adhesion force in that the fine-particles matter is omitted from a coat and a surface becomes low.

[0019] this invention approach explained above is an approach that the coat in which was characterized by using the striking power of the coat formation medium carried although it does not participate in coat formation as compared with above-shown JP,2-71872,A, and adhesive strength was excellent by this can be obtained. Moreover, it is the approach that this invention approach is formed by the resin which mixes an adhesion side together with other coat formation mixture as compared with above-shown JP,52-43731,A, and it is characterized by using the striking power of the coat formation medium carried although it does not participate in coat formation, and adhesive strength practically sufficient with little energy is obtained by this, and a precise coat can be obtained.

[0020] Condition (a) - (d) required in order to realize like the above coat formation faults is explained.

(a) Locally or on the whole, the adhesion matter needs to be in the condition of not hardening, in the first stage, even if few [like a coat formation fault]. If it is in the condition which the whole adhesion matter hardened [whole / coat formation fault] For example, formation of the adhesion matter layer in the processed member front face which serves as a forerunner of coat growth since there is almost no adhesive strength on the front face of a member of resin when the solid-state resin hardened completely is independently used in ordinary temperature does not take place. Moreover, since [of a between / fine-particles particles] it does not happen beginning to bleed, they are the adhesion matter, the fine-particles matter, a processed member, and a coat formation medium (mixing of the adhesion matter, the fine-particles matter, a processed member, and a coat formation medium is only hereafter called "coat formation mixture"). It stops at only being mixed.

[0021] (b) It is necessary to include a processed member and coat formation mixture needs to be made to vibrate or stir.

[0022] (c) Although a coat formation medium generates striking power and formation of a coat is carried, it does not become the component of a coat substantially in itself. Since a coat formation medium will be caught in a coat if a larger coat formation medium than a processed member cannot generate uniform striking power on the former front face and it is smaller than powder, a coat formation medium has a dimension substantially

smaller than a processed member, and needs for a dimension to be substantially larger than the powder matter. However, as long as it is 70% or less of range in a volume ratio, the bigger medium than a processed member may be contained. Moreover, when the direction on which striking power is centralized to some extent uses a spherical medium since press fit of fine particles advances well for example, the diameter of 1mm or more is more desirably desirable 0.5mm or more, and also when it is other configurations, it applies to this. Moreover, when each of media is replaced with the ball of this volume as a coat formation medium is smaller than a processed member, it says that the diameter is smaller than the greatest thing among the diameters of a processed member. Moreover, if requirements are filled with the average dimension to powder, desired striking power can be made. That is, if the former is larger than the latter with an average dimension in a part of particle used as a coat formation medium being finer than the fine-particles matter, desired striking power can be made. However, it is desirable for a medium finer than these fine-particles matter to have a possibility that it may be crowded for the inside of a coat, and not to be contained as much as possible.

[0023] The quality of the material of a coat formation medium needs to be satisfying the following requirements.

** There needs to be no big form status change-ization which observes a coat formation medium after coat formation by plastic deformation, and is accepted with the naked eye, and set like a comparison formation fault and elastic deformation should not become extremely large.

** It is divided and there are not a chip, rapid wear, etc. (there may be some wear by long-term use).

[0024] If the coat formation medium of the quality of the material which does not satisfy these requirements causes plastic deformation by the collision with a processed agent or causes extremely big elastic deformation like soft rubber, the blow dealt to the latter will be insufficient and desired coat formation will not take place. Moreover, if it is divided and a chip and rapid wear take place, the useful life longevity of a coat formation medium becomes short, and is uneconomical.

[0025] (d) Since the fine-particles matter is incorporated in a coat, it must be smaller than a leather curtain formation medium. Although especially the property of the fine-particles matter is not limited, in the case of resin powder, it is required to be resin more nearly hard than the adhesion matter which set like the coat formation fault and was stated by (a).

[0026] This invention which consists of above-mentioned requirements (a) - (d) is the coat formation approach in which the coat containing the fine-particles matter was formed, by adding vibration or stirring to a processed member, the adhesion matter like a coat formation fault which is in the condition do not harden, partially in the first stage at least, the fine-particles matter, and a coat formation medium within a container in the approach of sticking and forming a coat in a processed member front face.

[0027] In this invention as resin for adhesion matter Melamine resin, an epoxy resin, Phenol resin, furan resin, urethane resin, an unsaturated polyester resin, 1 liquid, such as polyimide resin and a urea-resin, or the thermosetting resin of 2 liquid hybrid model, Ultraviolet rays, such as an acrylic monomer with unsaturated polyester, partial saturation poly isocyanate, and a hydroxyl group, The resin hardened by the electron ray and other radiation irradiation, acrylic resin, polyester, Polyethylene, polyethylene terephthalate, polypropylene, a polyvinyl chloride, Thermoplastics, such as polyvinyl alcohol, nylon, polystyrene, and polyvinyl acetate, and those liquefied prepolymers or a monomer and the organic binder generally used for powder molding, for example, paraffin, camphor, etc. can be used. Moreover, natural products, such as gelatin, glue, and a Rhus verniciflua, can also be used as adhesion matter.

[0028] Moreover, since the adhesion matter needs to spread round the front face of a processed member at homogeneity, the above-mentioned resin for adhesion matter has the most desirable thing that is not half-liquid-like hardened [liquefied or]. Moreover, a fluidity is raised, and in order to spread over a member front face at homogeneity, an organic solvent or water can use a solid-state or the liquefied resin for adhesion matter, dissolving, diluting or distributing. In this case, since a solvent or water evaporates during mixing, adhesiveness increases gradually, and adhesion of fine particles takes place. However, if there are too many amounts of an organic solvent etc., it will become inadequate adhering to the processed member front face of the fine-particles matter. Moreover, thermoplastics is heated, increases a fluidity and adhesiveness and can be used. A solvent, water, etc. are evaporated from a coat during coat formation and after formation.

[0029] Furthermore, when a processed member contains resin like a resin bond magnet and a plastics member, add the solvent of the resin into coat formation mixture, resin is made to begin to melt from a processed member, and coat formation mixture can be supplied. The viscosity of resin is raised by evaporation of a solvent

etc. and the resin which once began to melt forms the resin coat which has adhesion on a processed member. [0030] Next, even formation of the fine-particles matter is the constituent of a ***** coat on a processed member. If it is resin, plastics, coating powder, etc. further and is various metals, alloy powder and ceramic powder, and the thing that has functions, such as corrosion prevention, fine sight grant, insulating grant, and improvement in on the strength, as fine-particles matter, various fine particles can be used.

[0031] If an example is given, as metal powder, there is alloy powder which makes a principal component powder, such as aluminum, Cu, Mg, Ti, Fe, Cr, Co, nickel, Zn, Pb, Sn, Rh, Ir, Pd, Pt, Ag, Au, Mo, and W, and them. All of these metals excel resin in reinforcement, and since there is little deterioration by water, salt water, etc., corrosion resistance is excellent. Since stainless steel, Cr, nickel, Mo, W, etc. make the firm passive state film on a front face, it excels in corrosion resistance. Therefore, these metals raise the reinforcement of a coat, and corrosion resistance. Since Rh, Ir, Pd, Ag, Au, etc. have a good fine sight and corrosion resistance when the place by which each metal is characterized is mentioned, it surpasses and the property of ** is given to a coat. Moreover, since Cu etc. has good corrosion resistance and good electrical conductivity, it is used for formation of an anticorrosion coat, formation of a plating primer coating layer, etc. good. nickel is also used for formation of a plating substrate etc. good. Zn and Sn carry out the corrosion prevention of almost all the metals according to the sacrificial anode effectiveness.

[0032] Ceramic powder is chemically more stable than a metal, and corrosion resistance is superior to the above-mentioned resin-metal compound coat. various kinds, such as a multiple oxide which makes the base an oxide, MgO and aluminum 2O₃, SiO₂, TiO₂, CrO₂, MnO₂ and Fe 2O₃, FeO and Fe 3O₄, CoO, NiO, CuO, ZnO, ZrO₂ and MoO, and them as these ceramics, and TiN, BN, -- various kinds, such as SiC, WC, TiC(s), etc., such as a stable nitride, -- stable carbide etc. can be used.

[0033] The above-mentioned metal, the above-mentioned ceramics, etc. may be contained in resin as a compounding agent, a pigment, etc. Moreover, two or more sorts of powder may be mixed and used.

[0034] When using resin powder as fine-particles matter, the powdered resin which made various heat coin nature resin, **** plasticity resin, and these distribute various pigments can be used.

[0035] The grain size of the fine-particles matter changes according to the magnitude of a processed member, the thickness of a coat, and the quality of the material of the fine-particles matter. In the case of the fine particles which cannot deform easily due to hard [, such as ceramic fine particles,], it is desirable for grain size to be small, and in the case of the metal powder which is rich in ductility, although it may be larger than this, generally, it is within the limits of 0.05-500 micrometers. 0.1-300 micrometers is within the limits of 0.1-100 micrometers more desirably. Generally, fine particles are easy to be caught with the adhesion matter, so that grain size is small. Moreover, the particle with a small grain size tends to be pushed in by blow between the particles of the fine-particles matter currently distributed on an adhesion matter coat, and sticking by pressure and association with the fine particles or the processed ingredient by plastic deformation tend to take place. Therefore, striking power is so small that the grain size of the fine-particles matter is small, and it ends, and the surface roughness of a coat also becomes small.

[0036] A coat formation medium can use a rigid plastic etc. for products made from the ceramics, such as iron, carbon steel, other alloy steel, copper and a copper alloy, aluminum and an aluminium alloy, other various metals, a product made from an alloy or aluminum 2O₃, and SiO₂, TiO₂, ZrO₂, SiC, and a glass pan. Moreover, hard rubber can also be used if sufficient striking power for coat shaping is applied. It is necessary to choose suitably the size of these coat formation medium, and the quality of the material according to the quality of the material of the configuration of a processed member and size, and the fine-particles matter to be used. Moreover, two or more sizes and the coat formation medium of the quality of the material can also be mixed and used. Moreover, they can also use depending on the case, being able to give surface treatment and surface coating. Moreover, the compound medium constituted with two or more above-mentioned ingredients may be used. Moreover, since relaxation and equalization of striking power are performed and the homogeneity of a coat and dispersion of film pressure are suppressed, elastic media, such as wood flour, and soft rubber, flexible plastics, may be suitably mixed in 50% or less of range of a volume ratio to said medium. Since these hardly produce striking power if they are independent, they are surely used together with said coat formation medium.

[0037] A globular shape, an ellipse form, a cube, the triangle pole, a cylinder, a cone, a triangular pyramid, a square drill, rhombohedron, an indeterminate form object, and other various configurations can be used for the configuration of a coat formation medium.

[0038] The rate of each component (element) of coat formation mixture determines that it does not incline

toward one of elements, but the whole balances so that an operation of a request of each component may be demonstrated. The amount of the fine-particles matter and the adhesion matter becomes settled with the sum total of the thickness of the coat given to a processed member, and the surface area of a processed member. However, as for the ratio of the adhesion matter and the fine-particles matter, it is desirable to convert into the volume after hardening of the adhesion matter, and to set up the rate for the adhesion matter in the fine-particles coat formed on one processed member to 0.5% or more. Adhering to the processed member of the fine-particles matter becomes being less than [this] inadequate. moreover, the mixing ratio of a coat formation medium and a processed member -- although it changes with configurations of a processed member, if a coat formation medium is not blended 20% or more by the apparent volume ratio at least, it is difficult for a rate for the homogeneity to a processed member front face and sufficient blow not to be performed, but to obtain a good coat.

[0039] Vibration or stirring within a container can be carried out by various approaches which are described below. The arm 3 (refer to drawing 1) which was prepared in the container 2 and fixed to the revolving shaft 4, the wing 5 (refer to drawing 2.) which fixed to the revolving shaft 4 Or although not illustrated, it is accomplished by agitators, such as an impeller and a blade. In addition, ten in drawing is coat formation mixture. Moreover, as shown in drawing 3, drum or pot-like container 2 the very thing may be rotated on a roller 6. As furthermore shown in drawing 4, the drum-like container 2 which fixed to the revolving shaft 4 may be rotated. The upper part may be released, the container may be sealed, or whichever is sufficient as it. In addition, a container 2 may be shaken as shown in drawing 5. You may stir during rocking. Moreover, the coat formation mixture 10 may be put in in the container 2 attached at the tip of the arm 7 which fixed symmetrically to the revolving shaft 4 shown in drawing 6, and the coat formation mixture 10 may be mixed with a centrifugal force. It is desirable to make a container 2 rotate. As long as actuation of a container 2 is the same, a rotational device may use the electrode holder of not only this but the shape for example, of a disk.

[0040] Or vibration may be added to the coat formation mixture 10 with the shaker 8 prepared in a container 2 and out of the container (refer to drawing 7). The magnitude of the force (exciting force) which takes an example to the approach of adding vibration below, and is applied to coat formation mixture is explained. The value (henceforth "exciting-force-ed"-dimensionless number -) which averaged exciting force by the gravity (henceforth "oscillating gravity") of a container and coat formation mixture becomes the index of the impulse force which a coat formation medium applies to a processed member. As an example, when it is weight-1kgf of a 2.8l. container, weight-10kgf of a steel ball (coat formation medium), and weight-1kgf of a processed member, oscillating gravity serves as 12kgf(s). At this time, the exciting force with the desirable period of 40Hz is 20-50kgf. Therefore, exciting force-ed is set to $1.67 (= 20/12)$ - $4.17 (50/12)$.

[0041] When using a larger container and it is weight-4.5kgf of a 20l. container, steel ball (coat formation medium) weight-70kgf, and weight-5.5kgf of a processed member as an example, oscillating gravity serves as 80kgf(s). At this time, the exciting force with the desirable period of 25Hz is 150kgf(s). Therefore, exciting force-ed is $150 / 80 = 1.88$.

[0042] Although a role 10 is sufficient as the upper limit of exciting force-ed when the processed member is made of the tough quality of the materials, such as a ferrous material, it is desirable to make the upper limit of exciting force-ed or less into five with the weak quality of the materials, such as a rare earth magnet, a bond magnet, ceramics, and glass. Moreover, as for especially the minimum of exciting force-ed, it is [one or more] desirable that it is 1.5 or more. If exciting force-ed is smaller than this minimum, a coat growth rate will become slow, on the other hand, when larger [than an upper limit] and a processed member is the weak quality of the material, that destruction becomes easy to take place, and deformation of a coat formation medium also becomes easy to take place. Although especially the frequency of vibration is not limited, it is desirable that it is the range of 2Hz - 200Hz. The amplitude at this time goes into the range of the above-mentioned exciting force-ed by 0.5-10mm.

[0043] Then, in the case of a stirring method, it is desirable for the centrifugal force generated by rotation to be so much contained in the range of the above-mentioned exciting force-ed at the sum total weight of coat formation mixture and a container. However, if a rotational frequency is too large and the volume rate of the coat formation mixture in/or a container is too large, coat formation mixture will be pushed against a vessel wall, and mixing will not fully take place. Therefore, as for 60 or less rpm and/, or the aforementioned volume rate, it is [a rotational frequency] desirable to fulfill 80% or less of conditions.

[0044] The equipment furthermore shown in drawing 8 as an excitation method can be used. Vibration exciter 8

is attached in the inferior surface of tongue of 20, and it is with the shape of U character which attached the 1-20-degree inclination preferably, and is as while adding vibration to the coat formation mixture 10, and 20 tops are slid down. A cross-section configuration is not limited to U typeface, but can use the thing of various configurations, such as circular, V typeface, and a square shape. Moreover, the upper part of a flume 20 does not necessarily need to be released. The vibrating screen 22 is installed down the lower limit of a flume 20. The vibrating screen 22 is smaller than the processed member 23, fixes a larger mesh than the coat formation media 24, such as a steel ball, to a frame etc., and it connects it with vibration exciter while making the whole incline. Therefore, among the coat formation mixture 10 which fell on the vibrating screen 22, the coat formation medium 24 passes through a mesh, and falls caudad, and, on the other hand, the processed member 23 is conveyed on the vibrating screen 22. The coat formation medium 24 is recovered by the medium recovery conveyor 30 which the vibrating screen 22 formed caudad, and a reuse is carried out to coat formation use. Moreover, the processed member 23 is recovered by the recall conveyor 31 formed in the bottom edge of the vibrating screen 22. If the above equipments are used, continuation full automatic-ization of coat formation will be attained. Furthermore, a flume 20 can be made into the shape of a ** face crease or a whorl as shown in drawing 9, and occupancy area of a flume 20 can be lessened. If it is with this ** face crease and outlet 20a of 20 is brought just under insertion section 20b of the coat formation mixture 10, the return path when carrying out the return of the coat formation medium can be shortened. Moreover, although illustration has not been carried out, it can hold a flume in a container and can also vibrate it the whole container.

[0045] the container with which the coat formation medium was held beforehand is made to vibrate or stir as insertion sequence to the container of each component of coat formation mixture, a coat formation medium is mixed, and it is in the container which a coat formation medium is mixing serially about a processed member, the fine-particles matter, and the adhesion matter -- it is -- inserting in coincidence is desirable. According to this approach, homogeneity mixing extent is raised. Although a coat formation medium is beforehand invested into a container here, and adhesion of the adhesion matter required for coat formation is brought about by what vibration or stirring is added for and striking power can be generated, the insertion sequence of other processed members, the fine-particles matter, and the adhesion matter, a count, the independent charge, the coincidence charge, etc. is completely arbitrary. If the resin which contains a pigment as the approach of the coincidence charge is inserted in, the fine-particles matter and the adhesion matter will become a container with the coincidence charge.

[0046] However, when as follows, special insertion sequence is desirable. ** When the resin melted into a solvent and resin fine particles (fine-particles matter) are used for liquefied resin or a solvent pan : beforehand, if only these and resin fine particles are mixed, in being easy to dissolve resin fine particles in liquefied resin, powdered condensation will tend to take place, and a uniform coat will not be obtained. Therefore, when powdered resin is inserted in a container in a late stroke or it inserts in a container previously, the liquefied resin inserted in later is inserted in a processed member and coincidence. ** When either of the components of coat formation mixture is heated : insert in resin after inserting in a container the processed member and the heated coat formation medium which inserts in the processed member which inserted in; resin which inserts in resin after heating a processed member and inserting in a container, and which carried out afterbaking and of which; heating was done.

[0047] By stiffening the adhesion matter during vibration or stirring, the fixed force of the fine-particles matter caught by the adhesion matter layer can be heightened. It is made to harden with a curing agent as the approach of hardening of the adhesion matter using 2 liquid hybrid model room-temperature-setting type resin, or heat hardening mold resin is stiffened with heating. Moreover, the approach of making it harden by the radiation irradiation of ultraviolet rays, a gamma ray, an electron ray, or others further etc. of evaporating a solvent is possible.

[0048] Furthermore, coat formation mixture other than the fine-particles matter can be beforehand mixed within a container, and the fine-particles matter can be inserted in in a container afterwards. The advantage by this approach is as following ** - **.

[0049] ** By spreading equally enough over a processed member front face resin with a large fluidity which was diluted especially with the solvent, a resin coat equal enough can be made and it can cover with the fine-particles matter to homogeneity.

[0050] ** the coat near the interface with the processed member used as a substrate -- the adhesion matter -- being rich (rich) -- becoming -- the front face of a coat -- the fine-particles matter -- being rich (rich) -- it

becomes and the transition layer where the rate of these components changes continuously exists within a coat. Therefore, the adhesion force of a coat becomes high.

[0051] ** Near the front face of a coat, the fine-particles matter is pressed fit, and depending on 70 to 90 volume %, and the case, the rate of the fine-particles matter is almost very as high as 100%, and exceeds the rate of pigment combination of a resin paint film you to be Haruka. Therefore, when the fine-particles matter is TiO_2 , MgO , Fe_2O_3 , etc. which are used as a pigment of a coating, in a coat front face, the engine performance which intercepts water and other corrosion components becomes very good. Usually, although the multilayer coating of the paint film is carried out and the amount of a pigment is made [many] in resin paint for corrosion prevention, this requires time and effort, and in interlaminar peeling, it becomes empty and it has a lifting and the problem to which thickness becomes large. By this invention method, a coat with many pigments can be obtained by one processing, and there is an advantage that thickness is thin.

[0052] The adhesion matter layer is beforehand formed in the processed member, and the processed member, coat formation medium, and fine-particles matter with which the adhesion matter layer was formed can be made to vibrate or stir after that in this invention. Therefore, the exception method of this this invention forms a coat in a processed member by adding vibration or stirring to the processed member, fine-particles matter, and coat formation medium by which the adhesion matter layer like a coat formation fault which is in the condition of not hardening, partially in the first stage at least was formed within a container.

[0053] Before being inserted in the container mentioned above, the adhesion matter layer beforehand formed in the processed member acts like the adhesion matter layer formed in the processed member with the non-hardened adhesion matter inserted in the container, and catches the fine-particles matter. If it is immersed in a solvent and this is pulled up case [whose processed member is / like a resin bond magnet or a plastics member], the resin near the front face of a resin bond magnet or a plastics member begins to melt, and an adhesion matter layer can be made easily.

[0054] Furthermore, in case the exception method of this invention is enforced, the fine-particles matter can be sprinkled on an adhesion matter layer (that is, the fine-particles matter is pasted up using the adhesion force which the adhesion matter layer has), and the method according to account of the Gokami can be enforced.

[0055] In case the exception method of this invention is enforced, said adhesion matter (first adhesion matter) and congener, or the adhesion matter (second adhesion matter) of a different kind can be added into coat formation mixture. The second adhesion matter flows on the adhesion matter layer already formed, makes a layer, grows and brings about association between fine-particles matter-adhesion matter. The adhesion matter mentioned above can be used as this second adhesion matter.

[0056] After mixing in this invention, by hardening the adhesion matter in the coat of the processed member in which the coat was formed, a coat can be made to be able to strengthen and adhesion can be improved again. Hardening is left in the ordinary temperature which is in a mixed container or heats a coat to the polymerization temperature of the adhesion matter out of a container, and is performed by evaporating a solvent etc. This hardening processing is effective, also when forming a coat by this invention approach on it further by making into a substrate the coat formed when a film strength, adhesion, etc. were inadequate and obtaining a multilayer coat. Furthermore depending on the class of adhesion matter, it can also harden with ultraviolet rays or a gamma ray, an electron ray, etc.

[0057] Immediately after coat formation, many fine-particles matter which is not fixed to a it top may remain (the fine-particles matter [**** / on a coat / un-] which separated is only hereafter called "residual fine particles".), and when using the processed member by which the coat was formed in electrical and electric equipment, electronic parts, or a precision machinery component etc. which dislikes dust and dust of this invention, it is necessary to remove these residual fine particles. Therefore, it is desirable to remove the residual fine particles from which un-fixing is isolated by approaches, such as spraying of ultrasonic cleaning and air. As for the hardening front stirrup of the adhesion matter, next either can carry out removal of such residual fine particles.

[0058] It is also possible to rub a coat front face by the elastic medium in removal of residual fine particles. for this reason -- being alike -- residual fine particles are removable by mixing within a container the processed member in which an elastic medium and an elastic coat were formed, having added vibration to the container enough, and stirring the processed member in which an elastic medium and an elastic coat were formed. By this approach, according to the shearing force between an elastic medium and residual powder, residual fine particles are removed and, in addition, the front face of a coat is polished. As for this approach, an appearance

with it is acquired. [the large and removal effectiveness of residual powder and] [more beautiful than ultrasonic cleaning] Therefore, it is suitable when using the member of this invention for an ornament supply and a sheathing supply.

[0059] As the above-mentioned elastic medium, since itself has impact absorptive power to some extent, what does not damage the coat which gave striking power strong against a processed member, and was formed, or is not shaved off deeply is desirable. For example, saw dust, wood powder, walnut **, flexible plastics, rubber, etc. are desirable. Furthermore oil etc. can be infiltrated into saw dust etc. and the effectiveness or rust-proofing nature of surface polish can also be raised.

[0060] Moreover, it can heat-treat to the processed member after the coat formation concerning this invention. As for this purpose, one is hardening of the adhesion matter. Although the curing temperature of the adhesion matter changes with classes of adhesion matter, generally it is 30-200 degrees C, and the setting time is about 1 - 500 minutes. The adhesion matter can be stiffened by performing heat treatment of this temperature and time amount.

[0061] Other purposes of heat treatment are increasing the particles of the fine-particles matter, or the bonding strength between the fine-particles matter and a processed member by thermal diffusion. It is considering as the coat which the pinhole of a coat was furthermore decreased and continued as much as possible. Moreover, homogenization of the membrane quality by diffusion between each class of multilayers and improvement in corrosion resistance or a mechanical property may be meant.

[0062] More than $M_p (1/3)$ of the temperature of heat treatment is desirable at below the melting point ($M_p:K$) of the fine-particles matter. if heat treatment temperature exceeds the melting point of the fine-particles matter - the fine-particles matter -- melting -- a molten bath -- joining of who or members is started. The target effectiveness will be hard to be acquired if heat treatment temperature is lower than one third of the melting points. Since this heat treatment temperature must naturally be lower than the melting point of a processed member, this approach is applied to the processed member which consists of matter with the melting point higher than heat treatment temperature.

[0063] The above-mentioned heat treatment is effective when the fine-particles matter is a low-melt point point comparatively like Zn, Sn, or these alloys. That is, although these Zn etc. can carry out the corrosion prevention of almost all the metals according to the sacrifice corrosion prevention effectiveness, it is required for coat structure to be close to the continuation film for that purpose. Although the sacrifice corrosion prevention effectiveness is not fully demonstrated in severe corrosive environment which is continuously exposed to storm sewage and salt water in the coat which the fine-particles matter obtained by this invention approach distributed, the sacrifice corrosion prevention effectiveness which gives corrosion resistance good enough is acquired by heat treatment. Although the coat of Zn and Sn had been conventionally formed of electroplating or hot dipping, since the former was a wet process, it had waste water and the problem of by-product processing, plating thickness was as thick as 100 micrometers or more, and a thin coat was not obtained, but the latter had the problem of not being suitable in the bit and piece again. On the other hand, since this invention method can form a thin coat in a bit and piece according to a simple dry process, it is suitable for the field of the corrosion-resistant coat formation accompanied by a problem by electroplating or hot dipping.

[0064] Furthermore, although it can heat-treat in atmospheric air when the fine-particles matter is matter with high corrosion resistance, such as aluminum and Sn, it is desirable to heat-treat in a vacuum or inert gas.

[0065] Moreover, the protective film of resin can also be given to the front face of the above-mentioned coat. This approach is effective in raising the reinforcement of a coat, and corrosion resistance, when applied to the coat which does not heat-treat. Even if there are few pitches and they remove residual fine particles, the powdered fixed force of the front face of a coat is in addition weak. Since the processed member in which the coat was formed by this invention approach does not have the intention of the use as a **** member, the force is not continuously applied to a coat from the exterior, but when under handling and a member are attached in a machine and impulse force and the strong force are applied from the exterior to inside, the fine-particles matter may be omitted or a coat may be destroyed locally. In order to prevent such un-arranging, it is effective to give the coat of resin. The coat of resin smooths a front face, and a fine sight also raises it, it fills a pinhole further, and bars osmosis of moisture.

[0066] If resin covering is applied to the coat which heat-treated, high heat treatment temperature cannot be taken, but this can be sealed and closed, when full removal of a pinhole etc. is difficult, or when air bubbles and a crack arise during heat treatment.

[0067] Although the approach of resin covering formation may make a spray or a processed member immersed into resin, it can form covering in the processed member in which the coat was formed as the dimension mentioned above substantially by adding vibration or stirring to a small coat formation medium and the resin for covering formation within a container thinly rather than a processed member at homogeneity. The coat formation medium (it is called a "covering formation medium".) for covering the processed member in which such a coat was formed applies the principle of the coat formation medium used for coat formation of the processed member mentioned above to covering formation of the processed member in which the coat was formed.

[0068] Paint of the usual coating containing a pigment can also perform resin covering to the processed member in which the coat furthermore mentioned above was formed. In this case, in addition to the effectiveness of resin covering, a good fine sight can be obtained.

[0069] Moreover, as a protective film, the plating of a metal or an alloy or the distributed plating (electroplating or electrolysis plating) of a metaled nonmetal other than a resin coat can be performed. It was difficult to perform electroplating directly as substrates are non-conductive matter, such as ceramics and plastics, conventionally or conductivity is the bad uneven matter like a resin bond magnet, and complicated pretreatment was required though it was possible. Therefore, after carrying out nonelectrolytic plating to the substrate, generally the cost which performs electroplating, and the method of taking time and effort were performed. on the other hand, this invention -- a substrate -- a metal -- since **** which gives a rich (rich) layer firmly and easily is made, electroplating of the non-conductive matter becomes very easy.

[0070] Moreover, even if it was the matter which can be galvanized conventionally, it was difficult to adjust the presentation of plating alloy metallurgy group-nonmetal composite coatings in the large range. On the other hand, since this invention forms a coat with a non-electrochemical process, its range of presentation accommodation is very wide.

[0071] Moreover, conventionally, by the chemical reaction of the plating electrolytic solution and a processed member, plating is difficult or there was a case of being impossible. This invention makes plating possible easily, also when starting. There is plating to a powder metallurgy ingredient as the example. Since this has pore, if it makes the plating electrolytic solution contact, plating liquid will permeate even the interior and electrodeposition will take place to internal corrosion or the interior of un-wanting. Although what is necessary is to have formed the metallic film upwards by PVD etc. and just to galvanize, in order to avoid this, PVD needs large-scale equipment. On the other hand, according to this invention method, the substrate of plating can be made by the very easy approach. Although activity light metals, such as Ag and Mg, or those alloys were not able to be galvanized if the member to plating liquid melted, **** happened and they did not perform special pretreatments, such as zincate processing, according to this invention method, plating to such a member is also enabled by the easy approach.

[0072] Since, as for the fine-particles matter coat of this invention used as the substrate of a plating coat, some pinholes are formed in the gap of the particle of the fine-particles matter etc., a pinhole may be formed also in a plating coat. in this case -- or it thickens a plating coat a little -- or the substrate of a plating coat -- a nonelectrolytic plating coat -- **** -- the pinhole in a plating coat can be prevented by forming thinly.

[0073] It is very advantageous if this invention approach is applied to coat formation to the rare earth sintered magnet and rare earth resin bond magnet as a processed member. Before explaining the advantage, the conventional technique is explained per a **** magnet and its protective film.

[0074] As for the outstanding magnetic properties, therefore need, the increment of a rare earth permanent magnet is being enhanced. Almost all the rare earth permanent magnets by which current production is carried out are the Sm-Co system which uses Sm and Co as a principal component, and a Nd-Fe-B system, and the resin bond magnet combined with what depended on sintering as a manufacturing method, and resin is almost the case. After a resin bond magnet presses the approach of performing compression molding after mixing resin with magnet powder, and hardening resin after that, an injection-molding method, and magnet powder, it is manufactured by the approach of infiltrating resin etc. since the **** magnet contains the activity ***** element so much -- an elevated temperature -- if used in a humid environment, dispersion in the performance degradation by corrosion or the engine performance will be produced, and the quality of a corrosion product will serve as a pollution source. In order that especially a Nd-Fe-B magnet may use iron as a principal component, corrosion resistance is low, grant of a protective coating is indispensable, and ***** and electropainting, such as an epoxy resin, are performed [as opposed to / in current and nickel plating / sintering

and a resin bond magnet] as opposed to the sintered magnet. However, nickel plating performed to a Nd-Fe-B sintered magnet with many bits and pieces also has the problem that plating actuation is troublesome, or there are problems, such as waste fluid processing, as the galvanizing method was already explained, and also the adhesion of the plating by removal of the oxide of a substrate being inadequate is inferior. There are problems, like as paint of resin was also already explained, paint actuation takes time and effort.

[0075] Moreover, since a bond magnet has the cheap price, and multilayer paint of resin is not realistic, monolayer paint is in use. For this reason, the corrosion resistance of a resin bond magnet has stopped at level lower than a sintered magnet. as a cure of this fault dissolution, giving electroplating on a nonelectrolytic plating substrate is proposed -- **** (JP,3-116703,A-refer to) -- there is a problem which was mentioned above. If electropainting is used, corrosion resistance will improve a little from spray painting, but this also needs large-scale paint and a waste fluid processing facility, and in order to carry out by hanging to a fixture fundamentally, it serves as cost quantity. Furthermore, since a resin bond magnet is porosity much more, if it does not thicken nonelectrolytic plating fairly, it does not serve as a good substrate from a sintered product. Moreover, it is said that management of a bath presentation is very difficult for the nonelectrolytic plating liquid which uses a Nd-Fe-B system as a processed member.

[0076] The fine-particles-pitch powder coat formed in a rare earth magnet front face of this invention has the following advantages.

** In the case of a sintered magnet ;; coat formation conditions that surface treatment is not needed [as opposed to / especially / the conventional plating coat] are loose (that is, it is not necessary to set up conditions especially bearing a Nd-Fe-B magnet in mind). Corrosion resistance can be made good by distributing fine particles, such as a stable oxide, for example, TiO_2 , MgO , Fe_2O_3 , etc., in a coat, and making [many] the content especially on a coat front face to the conventional resin coat.

[0077] The result of having investigated the cross-section structure of the coat obtained by the approach of three in the example 1 which used TiO_2 fine particles and an epoxy resin for drawing 12 with the electron microscope photograph (one 10000 times the scale factor [a SEM image,] of this) is shown. What is visible in the shape of a particle by the whole coat is TiO_2 among drawing. An epoxy resin appears in the shape of a continuous phase in the upper part of a coat, the lower parts, and these middle. Moreover, it is shown that TiO_2 is mixing with resin the particle with the indistinct profile which is visible to the lower left side of a coat. The coats made by this invention approach have gathered very densely [fine particles] so that drawing 12 may show.

[0078] In the case of a resin bond magnet : ** As opposed to the conventional resin paint since about the same corrosion resistance as multilayers is acquired -- the conventional single phase resin coat -- ***** --; which improves sharply -- by this invention method for having formed the non-hardened resin coat beforehand to a processed member before mixing with a coat formation medium especially First, if the resin coat is formed in the resin bond magnet as a processed member, the fine-particles matter and resin are pressed fit in the hole of a resin bond magnet, a sealing effect will be large to a ** sake, for this reason corrosion resistance will improve to it. this invention coat which uses the conductive fine-particles matter to the conventional nonelectrolytic plating-electrolysis plating has very high industrial application possibility.

[0079] When a plating coat is formed on the fine-particles-pitch powder coat formed in the rare earth magnet front face of this invention, there are the following advantages.

** In the case of a sintered magnet (comparing with the conventional plating coat) : since the plating substrate layer by this invention method has stuck firmly with resin on a base material front face, the plating coat which was excellent in adhesion is obtained by choosing a plating substrate layer appropriately to the plating layer formed on it. Moreover, although the plating coat usually had some pinhole, since the direct base material front face is arrived at as these pinholes are the conventional plating coats, the corrosion component which invaded from the pinhole permeates the interface on a plating layer and the front face of a base material, and tended to cause film peeling etc. When the oxidizing zone remains especially on the base material front face, it is very easy to cause film peeling. However, by this invention method, since most corrosion components from a pinhole are altogether stopped by this substrate layer since the good resin of anti-corrosiveness and a powder-mixing coat exist under a plating coat, and it is not spread on a base material front face, film peeling is lost.

[0080] ** In the case of a resin bond magnet (comparing with the conventional nonelectrolytic plating) : generally the bath of nonelectrolytic plating is expensive, and since a large amount of costs start waste fluid processing etc., it serves as cost quantity. Moreover, several steps of adhesion force with a substrate is inferior to a resin coat. Moreover, generally thick-film-ization has limited nonelectrolytic plating to the thin film 5

micrometers or less difficultly, and since especially a bond magnet is a porous body, it gathers the pinhole of base material both sides, and serves as a very porous coat. Such film does not almost have the cutoff capacity of the corrosion component which permeates from the pinhole of the electrolysis plating film formed on it, and dispersion, such as film peeling, tends to produce it. Moreover, the plating liquid of nonelectrolytic plating tends to remain at the pinhole of a bond magnet, and becomes the cause of film peeling that this is also big. Nd system bond magnet which gave nonelectrolytic plating has not yet resulted in mass production for these troubles.

[0081] According to this invention method, the closure of the pinhole on the front face of a magnet is carried out with resin, and since it is firmly stuck to the metal layer which serves as a substrate of plating by this resin layer further, the plating coat formed on it also has good adhesion. In order that this substrate layer may prevent diffusion of the corrosion component on the front face of a magnet like **, the corrosion resistance excellent farther as a result than a conventional method is acquired.

[0082] Although how to form an adhesion matter layer with resin was explained by the approach explained above, the silicate represented by the adhesion matter of an inorganic system, for example, water glass, can form a glass coat in a processed member front face by being able to make it distribute the fine-particles matter, a coat formation medium, and a processed member uniformly and mix, and making it fall by temperature, the solvent, or water dilution, while mixing viscosity. Moreover, a glass coat can catch the fine-particles matter. Therefore, it can replace with resin or the inorganic adhesion matter can be used with resin.

[0083] Hereafter, an example explains this invention in detail.

[Example] Example 1

The powder for quenching bond magnets with a grain size [with the presentation of Fe81Nd13 B6] of 100 micrometers or less was used. this powder -- an epoxy resin -- 3wt(s)% -- in addition, it mixed, it pressed with the welding pressure of 5 ton/cm², and 220 22mm phix20mm phix10mm Plastic solids were acquired. This for 1 hour, and it considered as the resin bond magnet. [150 degrees C] Next, having carried out 10kg (***** consistency of 5kg/l.) injection of the diameter phi3.0mm shot, and adding vibration with a vibration frequency 2500c.p.m. (cycle per minute) and an amplitude of 5mm to a circular pot with a volume [of 2.8l.], and a depth of 150mm as a coat formation medium, as fine-particles matter, 20g of aluminum powder with an average grain size of 1 micrometer was thrown in, and vibration was added to aluminum powder for 5 minutes.

[0084] Next, it took out, after feeding 20 magnets which ****(ed) to the methyl ethyl ketone (MEK) which melted 10% (97% of resin, 3% of curing agents) of epoxy resins beforehand, and covered the front face by resin into the pot which the coat formation medium and fine-particles matter which were mentioned above are inserted in, and is vibrating and vibrating them for 15 minutes. Carried out 2hr heating at 120 degrees C, finally put into the pot of the same size with piece of walnut ** 2.0kg with a mean particle diameter of 2mm, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed. The conditions of RH estimated corrosion resistance for the magnet which formed the coat of 10 micrometers of average thickness (maximum of 5 micrometers, minimum value of 2 micrometers) by the above approach 85 degree-Cx90%. The result is shown in the left column of Table 1 as "1."

[0085] the same approach as the following -- however, it created at a time 20 magnets which changed the following conditions and covered powder, respectively. The result is shown in the left column of Table 1 as "2-11." It replaced with 2-aluminum powder and Cu powder whose mean particle diameter is 1 micrometer was used. It replaced with 3-aluminum powder and Tio2 powder whose mean particle diameter is 0.3 micrometers was used. It replaced with 4-aluminum powder and 2Oaluminum3 powder whose mean particle diameter is 1 micrometer was used. It replaced with 5-aluminum powder and the Mgo powder whose mean particle diameter is 2 micrometers was used. It replaced with 6-aluminum powder and 2OFe3 powder whose mean particle diameter is 2 micrometers was used. After replacing with 7-aluminum powder and forming the coat whose thickness is 5 micrometers using Cu powder whose mean particle diameter is 1 micrometer, nickel plating layer of 10-micrometer thickness was formed with electrolysis plating. Tio2 addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of an average of 10-micrometer thickness in 8-resin bond magnet (example of a comparison). Spray blasting of the phosphoric-acid zinc chemical conversion liquid was carried out to 9-resin bond magnet, after desiccation, spray painting of the epoxy resin whose Tio2 addition is 20% was carried out, the cure was carried out at 120 degrees C for 6 hours, and the paint film (single film) of 10-micrometer thickness was formed (example of a comparison). A coat was not given to 10-resin bond magnet, but it examined as it is (example of a

comparison). The 20-piece each humidity cabinet test of the resin bond magnet which formed various coats as mentioned above was carried out, and corrosion resistance was evaluated. Test condition: RH neglect (check item: appearance) result is shown in Table 1 85 degree-Cx90%. In addition, in Table 1, A-E shows the following criteria.

A With no total all *****.

B Macroscopically with no rusting. There is a spotted rust [whole] of the microscope order of less than 10%.

C There is a spotted rust which less than 10% of the whole understands visually.

D A little big rusting is 10% or more in less than 30% of the whole.

E There are rusting with the whole remarkable to 30% or more, a film blister, and peeling.

[0086]

[Table 1]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	B	C	D
2	A	B	B	C
3	A	A	B	B
4	A	A	B	C
5	A	A	B	B
6	A	A	A	B
7	A	A	A	A
8	B	C	E	—
9	A	B	D	—
10	D	E	—	—

[0087] Example 2

Bond magnet powder with an average grain size [with the presentation of $\text{SmCO}_{4.8}$] of 20 micrometers was used. this powder -- an epoxy resin -- 3wt(s)% -- in addition, it mixed, it pressed with the welding pressure of 5 t/cm², and 80 22mm phix20mm phix10mm Plastic solids were acquired. This for 1 hour, and it considered as

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the resin bond magnet. [150 degrees C] Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 20g of aluminum powder with an average grain size of 1 micrometer was thrown in, and vibration was added to aluminum powder and a shot for 5 minutes. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. After carrying out 2hr heating of the magnet at 120 degrees C and carrying out the cure of the epoxy resin, finally, with 2kg of walnut ** with a mean particle diameter of 2mm, put into the pot of the same size as the object for coat formation, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0088] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90% (check item-appearance). The result is shown in Table 2. In addition, criterion A-E in Table 2 is the same as criterion A-E of Table 1. The figure of front Naka and the left column means the following processings, respectively.

1 - Average thickness formed the coat which is 10 micrometers by the above-mentioned processing.

It replaced with 2-aluminum powder and TiO₂ powder whose mean particle diameter is 0.3 micrometers was used.

TiO₂ addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness in 3-resin bond magnet (example of a comparison).

A coat is not given to 4-resin bond magnet, but it examines as it is (example of a comparison).

[0089]

[Table 2]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	B
2	A	A	A	A
3	A	A	B	B
4	C	C	D	E

[0090] Example 3

The powder for bond magnets with a grain size [with the presentation of Sm (Co_{0.72}Fe_{0.2}Cu_{0.06}Zr_{0.03})_{8.3}] of 100 micrometers or less was used. To this powder, 3wt(s)% was added, the epoxy resin was mixed, compression formation was carried out with the welding pressure of 5 t/cm², and 100 22mm phix20mm phix10mm Plastic solids were acquired. This for 1 hour, and it considered as the resin bond magnet. [150 degrees C] Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it,

20g of Cu powder with an average grain size of 1 micrometer was thrown in, and vibration was added to Cu powder during 5 minutes, and a shot. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. Next, after carrying out 2hr heating of the magnet at 120 degrees C and carrying out the cure of the epoxy resin, put into the pot of the same size as the object for coat formation at the last with 2kg of walnut ** with a mean particle diameter of 2mm, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed. It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90% (check item-appearance). The result is shown in Table 3. In addition, criterion A-E in Table 3 is the same as criterion A-E of Table 1.

[0091] The figure of front Naka and the left column means the following processings, respectively.

1 - Average thickness formed the coat which is 10 micrometers by the above-mentioned processing.

It replaced with 2-Cu powder and the MgO powder whose mean particle diameter is 1 micrometer was used.

It replaced with 3-Cu powder and 2OFe₃ powder whose mean particle diameter is 1 micrometer was used.

TiO₂ addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness in 4-resin bond magnet (example of a comparison).

A coat was not given to 5-resin bond magnet, but it examined as it is (example of a comparison).

[0092]

[Table 3]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	B
2	A	A	A	A
3	A	A	A	A
4	A	A	B	B
5	B	C	C	D

[0093] Example 4

The powder for bond magnets with an average grain size [with the presentation of Sm₂Fe₁₇N₃] of 2.5 micrometers was used. To this powder, 3wt(s)% was added, the epoxy resin was mixed, compression formation was carried out with the welding pressure of 5 t/cm², and 80 22mm phix20mm phix10mm Plastic solids were

acquired. This for 1 hour, and it considered as the resin bond magnet. [150 degrees C] Next, having fed a diameter phi 3 and 10kg of 0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 20g of aluminum powder with an average grain size of 1 micrometer was thrown in, and vibration was added to aluminum powder and a shot for 5 minutes. Next, 20 magnets which were beforehand immersed in the epoxy resin (10% MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. After carrying out 2hr heating of the magnet at 120 degrees C and carrying out the cure of the epoxy resin, put into the pot of the same size as the object for coat formation at the last with 0.2kg of walnut ** with a mean particle diameter of 2mm, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0094] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90% (check item-appearance). The result is shown in Table 4. In addition, criterion A-E in Table 4 is the same as criterion A-E of Table 1.

[0095] The figure of front Naka and the left column means the following processings, respectively.

1 - Average thickness formed the coat which is 10 micrometers by the above-mentioned processing.

It replaced with 2-aluminum powder and TiO₂ powder whose mean particle diameter is 0.3 micrometers was used.

TiO₂ addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness in 3-resin bond magnet (example of a comparison).

A coat was not given to 4-resin bond magnet, but it examined as it is (example of a comparison).

[0096]

[Table 4]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	B	C
2	A	A	B	B
3	B	B	C	E
4	D	D	E	—

[0097] Example 5

Coarse grinding of the ingot with the presentation of Nd_{13.8}Dy_{0.4}Fe_{78.2}B_{7.6} was carried out so that a mean diameter might be set to 20 micrometers with a stamp mill, and it ground so that a mean diameter might next be set to 3.0 micrometers with a jet mill. Applying the magnetic field of 12kOe(s) to this pulverizing powder, it pressurized in a magnetic field and the 1.5t /of the directions of a right angle by the force of 2 cm in metal mold,

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and the green compact was obtained. After sintering this green compact at 1100 degrees C in a vacuum for 2 hours, aging treatment was carried out at 650 degrees C for 1 hour, and 120 sintered compacts were obtained. After grinding this sintered compact completely by the grinder, centrifugal barrel finishing dropped the corner and washing desiccation was carried out continuously. The dimension of a product was 20mm phi x 5mm discoid. Next, having fed 10kg of diameter phi 3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 20g of aluminum powder with an average grain size of 1 micrometer was thrown in, and vibration was added to aluminum powder and a shot for 5 minutes. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. After carrying out 2hr heating of the magnet at 120 degrees C and carrying out the cure of the epoxy resin, put into the pot of the size same [2kg of walnut ** with a mean particle diameter of 2mm] as the last, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0098] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90%. The result is shown in Table 5. In addition, criterion A-E in Table 5 is the same as criterion A-E of Table 1.

[0099] The figure of front Naka and the left column means the following processings, respectively.

1 - Average thickness formed the coat which is 10 micrometers by the above-mentioned processing.

It replaced with 2-aluminum powder and TiO₂ powder whose mean particle diameter is 0.3 micrometers was used.

After it replaced with 3-aluminum powder and mean particle diameter formed the coat using TiO₂ powder which is 0.3 micrometers (residual powder not removing), it was immersed in the epoxy resin (5%MEK solution), and mean particle diameter formed the coat again using TiO₂ powder which is 0.3 micrometers (residual powder not removing). Then, residual powder with walnut husks was continuously carried out [for 2 hours] the cure and removed at 120 degrees C, and average thickness formed the 20 micrometers (maximum of 27 micrometers, minimum value of 18 micrometers) coat.

After it replaced with 4-aluminum powder and mean particle diameter formed the coat using TiO₂ powder which is 1 micrometer (residual powder not removing), it was immersed in the epoxy resin (5%MEK solution), and mean particle diameter formed the coat again using TiO₂ powder which is 0.3 micrometers (the residue not removing). The epoxy resin (5%MEK solution) was immersed further after that, the residue by walnut ** was continuously carried out [for 2 hours] the cure and removed at 120 degrees C, and average thickness formed the 22 micrometers (maximum of 29 micrometers, minimum value of 20 micrometers) coat.

It replaced with 5-aluminum powder and 2OFe₃ powder whose mean particle diameter is 1 micrometer was used.

TiO₂ addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of 10-micrometer thickness in 6-resin bond magnet (example of a comparison).

A coat was not given to 7-resin bond magnet, but it examined as it is (example of a comparison).

[0100]

[Table 5]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	B	B	C
2	A	A	B	C
3	A	A	A	B
4	A	A	A	A
5	A	A	B	B
6	C	E	—	—
7	E	—	—	—

[0101] Example 6

Coarse grinding of the ingot with the presentation of $\text{SmCo}_{4.6}$ was carried out so that a mean diameter might be set to 25 micrometers with a stamp mill, and it ground so that a mean diameter might next be set to 4.0 micrometers with a jet mill. Applying the magnetic field of 12kOe(s) to this pulverizing powder, it pressurized in a magnetic field and the 1.5t /of the directions of a right angle by the force of 2 cm in metal mold, and the green compact was obtained. This green compact was sintered at 1210 degrees C in the vacuum for 2 hours, gradual cooling was carried out after that, and 80 sintered compacts were obtained. After grinding this sintered compact completely by the grinder, centrifugal barrel finishing dropped the corner and washing desiccation was carried out. The dimension of a product was 20mm phix5mm discoid. Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 20g of TiO_2 powder with an average grain size of 0.3 micrometers was thrown in, and vibration was added to **** for [TiO_2] 5 minutes. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. Put into the pot of the size same [2kg of walnut husks with a mean particle diameter of 2mm] as the last after 2hr heating at 120 degrees C, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0102] It created at a time 20 magnets which covered various powder with the same approach as the following,

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respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90%. The result is shown in Table 6. In addition, criterion A-E in Table 6 is the same as criterion A-E of Table 1.

[0103] The figure of front Naka and the left column means the following processings, respectively.

- 1 - The coat of 10 micrometers of average thickness was formed by the above-mentioned processing.
- 2 - The above-mentioned processing was performed twice and the coat whose average film pressure is 20 micrometers was formed.

TiO₂ addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of an average of 20-micrometer thickness in 3-sintered magnet (example of a comparison).

A coat was not given to 4-sintered magnet but it examined as it is (example of a comparison).

[0104]

[Table 6]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	B
2	A	A	A	A
3	A	A	B	B
4	B	C	D	D

[0105] Example 7

Coarse grinding of the ingot with the presentation of Sm (Co_{0.69}Fe_{0.2}Cu_{0.06}Zr_{0.03})_{7.3} was carried out so that a mean diameter might be set to 25 micrometers with a stamp mill, and it ground so that a mean diameter might next be set to 4.0 micrometers with a jet mill. Applying the magnetic field of 12kOe(s) to this pulverizing powder, it pressurized in a magnetic field and the 1.5t /of the directions of a right angle by the force of 2 cm in metal mold, and the green compact was obtained. This green compact was sintered at 1215 degrees C in the vacuum for 2 hours, solution-ization was performed at 1170 degrees C for 1 hour, 2hr aging after gradual cooling was carried out at 850 degrees C, and 80 sintered compacts were obtained. After grinding this sintered compact completely by the grinder, centrifugal barrel finishing dropped the corner and washing desiccation was carried out. The dimension of a product was 20mm phix5mm discoid. Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 1500c.p.m. and an amplitude of 5mm to it, TiO₂ powder with an average grain size of 0.3 micrometers was thrown in, and vibration was added to TiO₂ during 5 minutes powder, and a shot. Next, 20 magnets which were beforehand immersed in the epoxy resin (10%MEK solution), and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. After carrying out 2hr heating of the magnet at 120 degrees C and hardening an epoxy resin, put into the pot of the size same [2kg of walnut ** with a mean particle diameter of 2mm] as the last, it was made to vibrate for 5 minutes, and the powder of the

surplus which remained on the front face was removed.

[0106] It created at a time 20 magnets which covered various powder with the same approach as the following, respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90%. The result is shown in Table 7. In addition, criterion A-E in Table 7 is the same as criterion A-E of Table 1.

[0107] The figure of front Naka and the left column means the following processings, respectively.

1 - Average thickness formed the coat which is 10 micrometers by the above-mentioned processing.

It replaced with 2-TiO₂ powder and 2OFe₃ powder whose mean particle diameter is 1 micrometer was used.

It replaced with 3-TiO₂ powder and aluminum powder whose mean particle diameter is 1 micrometer was used.

TiO₂ addition carried out spray painting of the epoxy resin which is 20%, carried out the cure at 120 degrees C for 6 hours, and formed the paint film (single film) of an average of 20-micrometer thickness in 4-sintered magnet (example of a comparison).

A coat was not given to 5-sintered magnet but it examined as it is.

[0108]

[Table 7]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	A
2	A	A	A	A
3	A	A	B	B
4	A	A	B	B
5	B	C	D	D

[0109] Example 8

Following powder (b) (b) was fabricated by the die pressing method under the following welding pressure, and the 25mm phix20mm phix10mm ring-like green compact was created.

(b) aluminum-2.75wt%Li Gas atomization powder

Average grain size 20 micrometers

Welding pressure 2 ton/cm²

(b) Mg Gas atomization powder

Average grain size 20 micrometers

Welding pressure 2 ton/cm²

[0110] These green compacts were sintered at 600 degrees C in Ar ambient atmosphere for 6 hours. Each consistency of a sintered compact was 90% of true density. Every 20 following covering processings each were performed to the obtained sintered compact.

1. 10kg (apparent density of 5kg/l.) of diameter phi3.0mm shots was put into the circular pot with a volume [of 2.8l.], and a depth of 150mm, 20g was supplied, TiO₂ powder with an average grain size of 1 micrometer was vibrated for 5 minutes, and homogeneity was made to distribute TiO₂ powder. The conditions of vibration were 5mm in vibration frequency 2500c.p.m. and amplitude.

[0111] Next, the member covered by the resin film by being immersed in a sintered compact was beforehand supplied to the methyl ethyl ketone (MEK) which melted 10% (epoxy resin 97wt% and curing agent 3wt%) of pitches, and vibration was continued for 15 more minutes. After carrying out 2hr heating of this at 120 degrees C, the powder of the surplus which remained on the member front face was removed by supplying to said pot and pot of the same size with 2kg (average grain size of 2mm) (apparent density of 1kg/l.) of pulverized walnut husks, and making it vibrate for 5 minutes on the same conditions. Thickness was an average of 10 micrometers.

[0112] 2. About 5-micrometer Cu film was given by the same approach as above 1 (1 micrometer of diameters of Cu powder, 15g use). Then, an average of 10 micrometers (maximum of 14 micrometers, minimum value of 8 micrometers) nickel plating film was made to form with electrolysis plating.

[0113] 3. In this example (aluminum-Li, Mg), since aluminum and Mg have the ionization tendency very larger than nickel, nickel plating cannot be performed directly. Then, a member is immersed in commercial Zn permutation solution which consists of a sodium hydroxide, a zinc oxide, and another Rochell salt and minute amount additive, electrolysis nickel plating processing by the Watts bath was carried out, and an average of 10-micrometer nickel plating film was made to form after performing Zn permutation processing (zincate processing) to a front face.

[0114] 4. An average of 10-micrometer epoxy resin (carbon black 20% addition) coat was formed in the sintered compact by spray painting.

5. To the sintered compact, did not form the coat and it was examined.

above powder (**) -- it created at a time 20 sintered compacts which covered various powder with the approach of the above 1-5 using (**), respectively, and the conditions of RH estimated corrosion resistance 85 degree-Cx90% (check item: appearance). The result is shown in Table 8. In addition, criterion A-E in Table 8 is the same as criterion A-E of Table 1. Moreover, rust is regarded as aluminum of white powder, or the oxide of Mg. In the case of above 3, many film peeling considered to be based on the residual of plating liquid was seen.

[0115]

[Table 8]

		2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
<u>イ</u>	1	A	A	A	B
	2	A	A	A	A
	3	A	E	—	—
	4	B	D	E	—
	5	E	—	—	—
<u>ロ</u>	1	A	A	A	A
	2	A	A	A	A
	3	A	E	—	—
	4	B	D	E	—
	5	E	—	—	—

[0116] Example 9

Following powder (Ha) (d) was fabricated by the die pressing method under the following welding pressure, and the 20mmx20mmx5mm plate-like green compact was created.

(c) Fe-0.3%C Electrolysis annealing powder (average grain size of 50 micrometers)

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welding pressure 3 ton/cm²
 (**) -- aluminum-1%Si Gas atomization powder (average grain size of 25 micrometers)

Welding pressure 3 ton/cm²

In the vacuum, about (Ha), it sintered at 1300 degrees C, and sintered at 600 degrees C about (d) for 6 hours for 6 hours. The consistency of a sintered compact was [(Ha)] 90% about (d) 85%. Every 20 following covering processings each were performed to the obtained sintered compact.

1. Put 10kg (apparent density of 5kg/l.) of diameter phi3.0mm shots into the circular pot with a volume [of 2.8l.], and a depth of 150mm, and threw in 20g of 2OFe3 powder with an average grain size of 1 micrometer, it was made to vibrate for 5 minutes, and homogeneity was made to distribute 2OFe3 powder. The conditions of vibration were 5mm in vibration frequency 2500c.p.m. and amplitude.

[0117] Next, by being beforehand immersed in the methyl ethyl ketone (MEK) which melted 10% (epoxy resin 97wt% and curing agent 3wt%) of pitches, the member covered by the resin film was supplied and vibration was continued for 15 more minutes. After carrying out 2hr heating of this at 120 degrees C, the powder of the surplus which remained on the member front face was removed by supplying to said pot and pot of the same size with 2kg (average grain size of 2mm) (apparent density of 1kg/l.) of ground walnut **, and making it vibrate for 5 minutes on the same conditions. Thickness was an average of 10 micrometers.

[0118] About 5-micrometer Cu film was given by the same approach as 2.1 (1 micrometer of diameters of Cu powder, 15g use). Then, an average of 10-micrometer nickel plating film was made to form with electrolysis plating.

[0119] 3. An average of 10-micrometer nickel plating film was made to form a member with electrolysis plating after Zn permutation processing like an example 8-3 beforehand.

[0120] 4. Thickness made the epoxy resin coat (TiO220% addition) which is an average of 10 micrometers form by spray painting. 5. With No Covering

[0121] The neutral salt spray test (35 degrees C, 5%NaCl) by the JIS corrosion test approach was performed to the sintered compact which processed more than, and appearance observation was performed. The test result of the sintered compact which covered various powder with the approach of the above 1-5 is shown in Table 9 using above powder (Ha) (d). In addition, criterion A-E in Table 9 is the same as criterion A-E of Table 1. Moreover, in the case of above 3, the blister produced much (d)s (Ha) on the plating film.

[0122]

[Table 9]

		2 4 hr	4 8 hr	1 2 0 hr	2 4 0 hr
△	1	A	A	C	C
	2	A	A	A	A
	3	C	D	E	—
	4	C	E	—	—
	5	E	—	—	—
≡	1	A	A	B	C
	2	A	A	A	A
	3	C	D	E	—
	4	B	C	E	—
	5	E	—	—	—

[0123] Example 10

The following nonmetal members a and b were created.

a. The following raw material was mixed, and powder compacting of the nickel-Zn ferrite sintered compact (it is 98% to consistency-true density) was carried out, it was sintered, and was obtained.

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NiO:Fe₂O₃:ZnO=20:50:30 (mole ratio). The sintered compact was cut and ground and 15mmx15mmx5mm Brock was obtained.

b. The following raw material was mixed, and powder compacting of the Sr ferrite sintered compact (it is 98% to consistency-true density) was carried out, it was sintered, and was obtained. SrCO₃: Fe₂O₃=1:5.9 (mole ratio). The sintered compact was cut and ground and the 15mm phix4mm cylinder was obtained.

[0124] The next coat processing was performed to these nonmetal members a and b.

1. TiO₂ coat was formed by the same processing as an example 8. (Drawing 10, A-**, B-**)

2. Spray painting of the epoxy resin (TiO₂20% addition) was carried out. (Drawing 10, A-**, B-**)

It cut after processing and the thickness part blanket-like voice on a nonmetal member was observed under the microscope. A result is shown in drawing 10. From drawing, it attaches and it understands this invention method 1 for the paint with them to be possible in the corner section. [the thin surroundings and] [more uniform than a conventional method 2]

[0125] Example 11

Metal mold shaping of the plastics member of a hemispherical bowl mold with a diameter [of 40mm] and a thickness of 2mm was carried out. 10kg of diameter phi3.0mm shots is put into a circular pot with a volume [of 2.8l.], and a depth of 150mm, 10g of Cu powder with an average grain size of 1 micrometer was thrown in, and it was vibrated for 5 minutes. Next, the methyl ethyl ketone (MEK) was sprayed all over the member, the front face was made into adhesiveness, it invested in said pot, and vibration was continued for 15 minutes. After taking out the plastics member after that and carrying out 2hr heating at 50 degrees C, put into another pot of the same size with 2kg (particle size of 2mm) of pulverized walnut husks, it was made to vibrate for 5 minutes, and the residual powder on the front face of a member was taken and removed.

[0126] About 4-micrometer Cu layer was able to be formed in the member front face by this, the resistance of the front face which was infinite before processing was able to decrease to 0.2 - 0.5 ohm/cm, and nickel plating was able to be easily performed using the usual Watts bath. Although the tape test was performed to the member after plating, exfoliation did not take place.

[0127] Example 12

The following processing was performed to 100 glass pieces of the heart mold shown in drawing 11. When the MECHINO the chill ketone (MEK) solution was used as resin 1.5%, and also 5g of gold dust with a mean particle diameter of 1 micrometer was invested by the same processing as an example 8 and it was made to vibrate for 15 minutes, about 2-micrometer beautiful ***** was given. Exfoliation was not seen in a tape test.

[0128] 2. About 10-micrometer Cu leather ** was given by throwing in 20g of Cu powder with a mean particle diameter of 1 micrometer, and making it vibrate by the same processing as an example 8 for 15 minutes.

Thereby, the surface electrical resistance of a member became 0.2 - 0.5 ohm/cm, and changed into the condition in which electroplating is possible enough. The glossy very beautiful front face was obtained by giving about 2-micrometer gilding with electrolysis plating succeedingly.

[0129] Example 13

Coarse grinding of the ingot with the presentation of Nd_{13.8}Dy_{0.4}Fe 78.2B7.6 was carried out so that a mean diameter might be set to 20 micrometers with a stamp mill, applying the magnetic field of 12kOe(s) to pulverizing powder so that a mean diameter may next be set to 3.0 micrometers with a jet mill, it pressurized in the magnetic field and the direction of a right angle by the force of 1.5 t/cm² in metal mold, and the green compact was obtained. After sintering this green compact at 1100 degrees C in a vacuum for 2 hours, aging treatment was carried out at 650 degrees C for 1 hour, and 60 sintered compacts were obtained. Washing desiccation was carried out, after grinding this sintered compact completely by the grinder and centrifugal barrel finishing dropped the corner. The dimension of a product was 20mm phix5mm discoid. Next, having fed 10kg of diameter phi3.0mm shots into the with a volume depth [150mm depth of 2.8l.] circular pot, and adding vibration with a vibration frequency 2500c.p.m. and an amplitude of 5mm to it, 30g of tin powder with an average grain size of 1 micrometer was thrown in, and vibration was added to tin powder and a shot for 5 minutes. Next, 20 magnets which were beforehand immersed in the paraffin MEK solution 5%, and covered the front face by resin were thrown in, and it took out, after making it vibrate for 15 minutes. Finally put into the pot of the same size with piece of walnut ** 2kg with a mean particle diameter of 2mm, it was made to vibrate for 5 minutes, and the powder of the surplus which remained on the front face was removed.

[0130] Next, the member was heated and taken out in the 4-hour vacuum at 300 degrees C, and the conditions of RH estimated corrosion resistance 85 degree-Cx90% (check item: appearance). The result is shown in Table

10. In addition, criterion A-E in Table 10 is the same as criterion A-E of Table 1.

[0131] The figure of **** of a table means the following processings.

1 Tin Processing Article (Average Thickness 10 Micrometers)

2 10 Micrometers of Spray Painting (Epoxy Resin; 2 20% Addition of TiO(s)) Average Thickness

3 With No Processing

[0132]

[Table 10]

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	A
2	C	E	—	—
3	E	—	—	—

[0133]

[Effect of the Invention] Since this invention can give the fine-particles coat excellent in corrosion resistance and adhesion to various members by the simple approach as explained above, the applicability of a fine-particles coat is expanded conventionally. Furthermore, the corrosion resistance which was excellent by applying this invention method to the processed member from which corrosion resistance conventionally sufficient by resin paint is not acquired can be acquired.

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the example which performs churning by this invention by the arm.

[Drawing 2] It is drawing showing the example which performs churning by this invention by feather, and is **.

[Drawing 3] It is drawing showing the example which performs churning by this invention by rotation of a tumbler.

[Drawing 4] It is drawing showing the example which performs churning by this invention by rotation of a cylinder container.

[Drawing 5] It is drawing showing the example which performs churning by this invention with rocking of a cylinder container.

[Drawing 6] It is drawing showing the example which is made to rotate a container around a revolving shaft and performs churning by this invention.

[Drawing 7] It is drawing showing the example which performs vibration by this invention by the excitation of a pot.

[Drawing 8] It is drawing showing the example which performs vibration by this invention by the excitation of a flume.

[Drawing 9] It is drawing showing the example of a flume.

[Drawing 10] It is drawing in which attaching a coat and showing the surroundings.

[Drawing 11] It is drawing of a processed member.

[Drawing 12] It is the electron microscope photograph in which the structure of TiO₂ in a coat particle is

shown.

[Description of Notations]

2 Container

3 Arm

4 Revolving Shaft

5 Feather

6 Roller

8 Shaker

10 Coat Formation Mixture

20 Flume

22 Screen

24 Coat Formation Medium

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平5-302176

(43) 公開日 平成5年(1993)11月16日

(51) Int. Cl. ⁵

C23C 26/00

B05D 1/24

識別記号

Z

8720-4D

F I

審査請求 未請求 請求項の数18 (全22頁)

(21) 出願番号 特願平3-224782
(22) 出願日 平成3年(1991)8月9日

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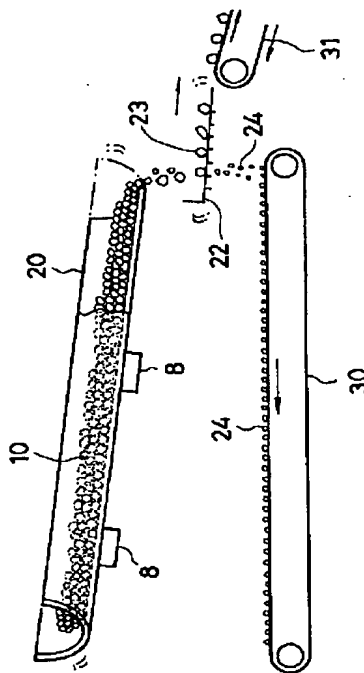
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(54) 【発明の名称】 皮膜形成方法

(57) 【要約】

【目的】 密着性にすぐれた粉体皮膜を簡便な方法で形成する。

【構成】 被処理部材23、皮膜形成の少なくとも初期において未硬化の状態にある樹脂、粉体物質、皮膜形成媒体24を加振又は攪拌8、10する。



【特許請求の範囲】

【請求項 1】 被処理部材表面に皮膜を密着して形成する方法において、被処理部材、皮膜形成過程の少なくとも初期において少なくとも部分的に未硬化の状態にある樹脂、粉体物質（皮膜形成過程において前記樹脂よりも硬質の樹脂粉末のこともある）、および前記被処理部材よりも寸法が実質的に小さくかつ前記粉体物質よりも寸法が実質的に大きい皮膜形成媒体に容器内にて振動または攪拌を加えることにより、粉体物質を含む皮膜を形成することを特徴とする皮膜形成方法。

【請求項 2】 前記容器内に予め皮膜形成媒体を入れ、振動又は攪拌を加えながら前記被処理部材、粉体物質及び樹脂を逐次あるいは同時に前記容器に装入することを特徴とする請求項 1 記載の皮膜形成方法。

【請求項 3】 前記樹脂を振動又は攪拌中に硬化させることを特徴とする請求項 1 から 2 記載の皮膜形成方法。

【請求項 4】 前記容器内にて皮膜形成媒体、前記被処理部材及び樹脂を混合し、さらに前記容器に粉体物質を装入して、振動又は攪拌を行うことを特徴とする請求項 1 から 3 までのいずれか 1 項記載の皮膜形成方法。

【請求項 5】 被処理部材表面に皮膜を密着して形成する方法において、皮膜形成過程の少なくとも初期において少なくとも部分的に未硬化の状態にある第一の樹脂からなる皮膜を施した被処理部材、粉体物質（皮膜形成過程において前記樹脂よりも硬質の樹脂粉末のこともある）、および前記被処理部材よりも寸法が実質的に小さくかつ前記粉体物質よりも寸法が実質的に大きい皮膜形成媒体に容器内にて振動又は攪拌を加えることにより、粉体物質を含む皮膜を形成することを特徴とする皮膜形成方法。

【請求項 6】 前記第一の樹脂と同種又は異種の樹脂であって皮膜形成過程の少なくとも初期において少なくとも部分的に未硬化の状態にある第二の樹脂を前記被処理部材、粉体物質及び皮膜形成媒体と混合することを特徴とする請求項 5 記載の皮膜形成方法。

【請求項 7】 前記被処理部材表面に皮膜形成後、該皮膜中の樹脂を硬化することを特徴とする請求項 1 から 6 までのいずれか 1 項記載の皮膜形成方法。

【請求項 8】 前記被処理部材表面に皮膜形成後、該皮膜の表面部に残留する遊離粉体物質を除去することを特徴とする請求項 1 から 7 までのいずれか 1 項記載の皮膜形成方法。

【請求項 9】 前記皮膜表面部の残留遊離粉体を除去する際に、該皮膜を形成した被処理部材表面を軟質の媒体により摩擦することを特徴とする請求項 8 記載の皮膜形成方法。

【請求項 10】 前記皮膜を形成した被処理部材に熱処理を施すことを特徴とする請求項 1 から 9 までのいずれか 1 項記載の皮膜形成方法。

【請求項 11】 前記皮膜を形成した被処理部材を前記

樹脂と同一のあるいは前記樹脂とは異なる樹脂で被覆することを特徴とする請求項 1 から 10 までのいずれか 1 項記載の皮膜形成方法。

【請求項 12】 請求項 1 1 記載の樹脂被覆を施す際に、前記被処理部材よりは寸法が実質的に小さい皮膜形成媒体及び該樹脂に容器内にて振動又は攪拌を加えることを特徴とする請求項 1 1 記載の皮膜形成方法。

【請求項 13】 請求項 1 1 記載の樹脂被覆を塗装により行うことを特徴とする請求項 1 1 記載の皮膜形成方法。

【請求項 14】 前記皮膜を導電性粉体物質を用いて形成した被処理部材に金属または合金の皮膜を形成することを特徴とする請求項 1 から 10 までのいずれか 1 項記載の皮膜形成方法。

【請求項 15】 前記金属または合金の皮膜を電気めっき又は無電解めっきにより形成することを特徴とする請求項 1 4 記載の皮膜形成方法。

【請求項 16】 前記被処理部材が希土類焼結磁石であることを特徴とする請求項 1 から 15 までのいずれか 1 項記載の皮膜形成方法。

【請求項 17】 前記被処理部材が希土類樹脂結合磁石であることを特徴とする請求項 1 から 16 までのいずれか 1 項記載の皮膜形成方法。

【請求項 18】 前記被処理部材、前記粉体物質、皮膜形成媒体と共に振動又は攪拌が加えられる樹脂の一部または全部に代えて無機粘着物質を使用することを特徴とする請求項 1 から 17 までのいずれか 1 項記載の皮膜形成方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は各種部材の表面に皮膜を形成する方法に関するものである。ここで言う各種部材とは、各種機械、自動車及びその他の車両、船舶、飛行機などに使用される機械部品、電気・電子部品、装飾用品、金具、磁石、玩具部品などであって、比較的小物部品である。また部材の材質は、金属、合金、金属間化合物、無機化合物、プラスチック、セラミックスなどである。また、各種部材はすでに表面に公知の各種皮膜が形成されているかあるいは表面改質が施されているもよい。

【0002】 また、本願発明の方法により形成する「皮膜」とは防食、機械的強度付与、絶縁層形成及び／又は美観付与を目的とし、さらに公知の各種皮膜を形成するための下地層の形成を目的とするものである。窒化チタンなどで周知な耐摩耗性用途、二硫化モリブデンなどで周知な潤滑性用途は本発明は対象としない。

【0003】

【従来の技術】 さらに本発明は粉体の皮膜を形成する方法の改良に関する。粉体の皮膜を形成する従来技術としては以下の方法が公知である。

【0004】①粉体塗装

この方法は、予備加熱した部材に粉体塗料を散布、噴霧、溶射などにより堆積し溶融させ、塗膜を得る方法である。この方法は溶剤を使用しないので、溶剤による公害がなくかつ省資源的である利点をもっている。この方法に関する特許文献としては、特開平2-258084号、特公昭57-13347号、特開昭53-29347号、特公昭58-37029号がある。また、粉体塗装は静電スプレー塗装によっても行われる。

【0005】②粉体被覆

この方法は被処理部材表面が接着性をもっているものと、非接着性である方法に分けられる。前者に属する特開平2-71872号によると、予め粘着性を与えた部材表面に粉体物質を接触させ、部材に振動を加えて部材表面に付着した粉体をかさ密度以下に圧縮し、その後部材に固着していない粉末を除去する方法が開示されている。部材としてはカラーテレビジョンのスクリーンが、粉体としては蛍光トナーが前記公報に具体例として示されている。

【0006】後者に属する特開昭52-43731号は、中空の金属製品内に金属または合金粉末及び球状もしくは粒状の硬質物質を入れ、この金属製品を回転もしくは振動させて、金属もしくは合金粉末を製品内面に被覆する方法を開示する。粉体は金属製品に圧着され、同時に振動に起因する熱エネルギーにより粉末の金属と製品の金属の間に拡散を起こさせることにより拡散接合も行われる。この方法によると中空製品の内面の耐熱性が向上することが謳われている。

【0007】③金属粉末圧延法

金属粉末を圧延板の表面に付着させ、ロール圧延により粉末を圧延板に圧着し、その後熱処理により拡散接合する方法である（特開昭52-33840、51-143531号、57-54270号、47-29232号参照）。

【0008】

【発明が解決しようとする課題】粉体皮膜の形成方法は、各種皮膜形成法に対して以下のような利点をもっている。電気めっきあるいは無電解めっき法に対して：酸、アルカリなどを使用しないために、処理廃液の処理が不要になるとともに、被処理部材が活性であっても、腐食等の問題が起こらない。溶融めっき法に対して：被処理部材を高温にさらすことが避けられる。

PVD、CVD法に対して：大掛かりな装置が不要、生産性が高い。

【0009】しかしながら、粉体皮膜を各種部材に適用するには皮膜に要求される性能が満足されるほかに、皮膜形成法の能率や信頼性が高いことが必要である。

【0010】③の金属粉末圧延法は被処理部材が板でありかつ圧延可能な材質に限られるので、機械部品などに

直接粉体皮膜を形成することはできない。

【0011】①の粉体塗装方法は、塗料の散布、スプレーなどにより粉体塗料を被処理部材に適用するが、被処理部材が小物であるときはそれを反転させる、あるいは鉤等に釣り下げるなどの操作が必要であるために、能率的とは言えない。また被処理部材を加熱することによる材質の劣化などがある材料には適用できないという問題がある。

10 【0012】②の粉体被覆法のうち特開平2-71872号公報に開示された方法は、粘着性表面に付着した粉体はある程度の付着力を有するが、その上にある粉末は粉末粒子相互の振動により粉末が圧縮されているにすぎないので、粉体被覆は外力がかかったときに脱落しやすく、また腐食性媒体が容易に浸透する隙間も多いために、防食などの目的には向かない。さらに、被処理部材が凹凸を有する場合は、凹部への粉体の付き回りが不良である。

20 【0013】②の粉体被覆法のうち特開昭52-43731号公報に開示された方法は、機械的結合（圧着）と拡散接合を同時に行うものである。このためには相当のエネルギーが必要であり、例えば実施例では加振力500kgの振動ミルや回転数300rpmの高速遊星ミルが用いられている。したがって、被処理部材は強度が高いことが必要であり、セラミックや強度の低いプラスチックなどは被処理部材とならない。また、酸化物等の脆い粉体は振動により破壊されるので、適用できない。

30 【0014】前掲特開昭52-43731号公報に開示された方法は、内面だけの被覆にしか適用できず、また相当の高エネルギーが必要であるために、本発明で言う各種部材に皮膜を形成する方法には採用できない。①の粉体塗装方法及び②の粉体被覆法のうち特開平2-71872号公報の方法は、各種部材への適用が可能であるが、上述のような問題があるために、本発明は、粉体被覆形成の能率を高めると共に、付着力が優れかつ緻密な粉体皮膜を形成することができる皮膜形成方法を提供することを目的とする。

【0015】

40 【課題を解決するための手段及び作用】本発明法における粉体皮膜形成法において従来法に比べて特長的なところは以下にある。樹脂、粉体物質及び被処理部材を皮膜形成媒体とともに容器内で振動又は攪拌すると、被処理部材表面にまず樹脂の層が形成される。この樹脂層の厚みは、粉体物質、樹脂、皮膜形成媒体、被処理部材の投入順序や混合の仕方によって変わり、例えば、樹脂と粉体物質の投入が同時に行われる場合は、部材表面と樹脂及び部材表面と粉体粒子の接触が同時に起こるために、部材表面に形成される樹脂単独の層は非常に薄くなるか、検出困難になることがある。

【0016】樹脂皮膜形成に続いて、粉体物質が樹脂層の粘着力により樹脂層に捕捉・固定される。同様に樹脂

層が被処理部材表面で硬化する時に粉体物質を捕捉して硬化する。振動又は攪拌を受けている皮膜形成媒体は、同様に振動又は攪拌を受けている粉体物質に打撃力を与え、前記粉体物質の粒子を既に樹脂層に捕捉され、押し込まれた粒子の間に圧入されるので、樹脂の粘着力等に加えて皮膜形成媒体の打撃力により一層強く粉体物質は固定される。また、一部被処理部材同志の衝突も起こり、同様に粉体物質の圧入が促進される。よって樹脂層には次第に多くの粉体物質が混合されるようになるとともに、樹脂層も厚くなるので、皮膜が成長し続ける。

【 0 0 1 7 】以上説明したように、樹脂と粉体物質の間に結合が作りだされる他に、粉体物質の粒子同志も皮膜形成媒体の打撃力を介して被処理部材表面で衝突するので、これらの間にも主として塑性変形とならびに副次的に摩擦熱による原子間拡散とによる結合力が作りだされる。特に、粉体物質が、Al, Cu, Zn, Sn, Au, Ag, Pb およびこれらの合金等のように延性に富む金属又は合金、あるいはプラスチックである場合は、衝突したこれら粉末粒子が塑性変形して、圧接のように接合される。またこのような接合は粉体物質と被処理部材の間でも起こる。この結果皮膜内の物質の構成は強固になる。粉体物質が非延性物質であると、粉体粒子間の結合と、これによる皮膜層形成は起こり難くなる。

【 0 0 1 8 】皮膜表面に衝突する皮膜形成媒体は粉体物質の粒子の間から樹脂を絞りだし、形成中の皮膜表面ににじみ出る。樹脂は皮膜形成媒体にも一部付着する。この樹脂は皮膜形成媒体が他の被処理部材表面に際衝突する際に、再び被処理部材表面にも付着する。かかる樹脂層表面に粉体粒子が付着する。このような樹脂の絞り出しと前述の皮膜成長が同時に進行する。しかし膜の成長と共に皮膜表面における粉体物質の割合が多くなる。すると皮膜形成媒体は皮膜表面における粉体物質に打撃を与えるで、粉体物質は凝集しそしてますます樹脂の割合は少なくなるとともに皮膜の成長速度が低下する。これは粉体物質が皮膜から脱落することと表層における付着力が低くなることによる。

【 0 0 1 9 】以上説明した本発明方法は前掲特開平 2 - 7 1 8 7 2 号公報と比較すると、皮膜形成に関与しないが媒介する皮膜形成媒体の打撃力を利用することを特徴とし、これにより接着力が優れた皮膜を得ることができる方法である。また、本発明方法は前掲特開昭 5 2 - 4 3 7 3 1 号公報と比較すると、接着面を他の皮膜形成混合物と一緒に混合する樹脂で形成し、皮膜形成に関与しないが媒介する皮膜形成媒体の打撃力を利用することを特徴とし、これにより少ないエネルギーで実用上十分な接着力が優れかつ緻密な皮膜を得ることができる方法である。

【 0 0 2 0 】以上のような皮膜形成過程を実現するために必要な条件 (a) ~ (d) を説明する。

(a) 樹脂は皮膜形成過程の少なくとも初期において局

所的または全体的に未硬化の状態にある必要がある。もし樹脂全体が皮膜形成過程の全体において硬化した状態であると、例えば、完全に硬化した固体樹脂を単独で常温で使用すると樹脂の部材表面への接着力がほとんどないため皮膜成長の先駆けとなる被処理部材表面における樹脂層の形成が起こらず、また粉体粒子間へのにじみ出しも起こらないため樹脂、粉体物質、被処理部材及び皮膜形成媒体 (以下、総称する場合は「皮膜形成混合物」と称する) が単に混合されるに留まる。「未硬化」とは皮膜中の樹脂に対し、溶媒の蒸発および／又はキュアリング等が終了し、最終的に使用される段階にある樹脂よりも軟質の状態にあることをいう。

【 0 0 2 1 】 (b) 被処理部材を含めて皮膜形成混合物が振動又は攪拌させられる必要がある。もし被処理部材を固定してその他の皮膜形成混合物を混合しながら被処理部材と接触させるならば、被処理部材全面に均一な皮膜を形成させることが困難になる。また、混合により皮膜形成媒体を被処理部材表面から離脱させて、皮膜形成に関与はするが媒介に留まるようにすることができる。

20 【 0 0 2 2 】 (c) 皮膜形成媒体は打撃力を発生して皮膜の形成の媒介をするが、それ自身は実質的に皮膜の成分にならない。被処理部材より大きい皮膜形成媒体は前者の表面上で均一な打撃力を発生することができず、また粉末よりも小さいと皮膜形成媒体が皮膜中に捕捉されてしまうので、請求項 1 に限定したような寸法の要件が必要である。ただし、体積比で 7 0 % 以下の範囲であれば、被処理部材よりも大きな媒体が含まれていてもよい。また、打撃力のある程度集中させる方が粉体の圧入がよく進行するため、例えば球状の媒体を使用する場合はその直径が 0 . 5 mm 以上、より望ましくは 1 mm 以上望ましく、他の形状の場合もこれに準ずる。また被処理部材よりも小さいときは、媒体の一つ一つを同体積の球で置き換えたとき、その直径が被処理部材のさしわたしのうち最大のものよりも小さいことを言う。また粉末に対しては、平均寸法で要件を満たしていれば、所望の打撃力をつくり出すことができる。すなわち、皮膜形成媒体となる粒子の一部が粉体物質より細かくとも、平均寸法で前者が後者より大きければ所望の打撃力を作り出すことができる。ただし、これら粉体物質より細かい媒体は皮膜中にとりこまれる恐れがあり、できるだけ含まれないことが望ましい。

【 0 0 2 3 】皮膜形成媒体の材質は次の要件を満たしている必要がある。

①塑性変形により皮膜形成前後に皮膜形成媒体を観察して肉眼で認められるような大きな形状変化がなく、かつ、皮膜形成過程において弾性変形が極端に大きくならないこと。したがって軟質ゴムなどはこの要件を満たさない。

②割れ、欠け、急激な摩耗などがないこと (長期的使用による若干の摩耗はあってもよい) 。

【0024】これらの要件を満たさない材質の皮膜形成媒体が被処理材との衝突により塑性変形を起こしたりあるいは軟質ゴムのように極端に大きな弾性変形を起こしたりすると、後者に与える打撃が不足して所望の皮膜形成が起こらなくなる。また、割れ、欠け、急激な摩耗が起こると、媒体の耐用寿命が短くなり、不経済である。

【0025】(d) 粉体物質は皮膜中に取り込まれるためには、皮膜形成媒体よりは小さくなければならない。粉体物質の性質は特に限定されないが、樹脂粉末の場合は皮膜形成過程において、(a) で述べた樹脂よりも硬質な樹脂であることが必要である。以下、各請求項を順にその構成及び作用に関して説明する。

【0026】上述の要件(a)～(d)からなる本発明は、被処理部材表面に皮膜を密着して形成する方法において、被処理部材、皮膜形成過程の少なくとも初期において少なくとも部分的に未硬化の状態にある樹脂、粉体物質(皮膜形成過程において前記樹脂よりも硬質の樹脂粉末のこともある)、および前記被処理部材よりも寸法が実質的に小さくかつ前記粉体物質よりは寸法が実質的に大きい皮膜形成媒体に容器内にて振動または攪拌を加えることにより、粉体物質を含む皮膜を形成することを特徴とする皮膜形成方法である(請求項1)。

【0027】本発明において、樹脂としては、メラミン樹脂、エポキシ樹脂、フェノール樹脂、フラン樹脂、ウレタン樹脂、不飽和ポリエステル樹脂、ポリイミド樹脂、尿素樹脂などの1液もしくは2液混合型の熱硬化性樹脂、不飽和ポリエステル、不飽和ポリイソシアネート、水酸基をもつアクリル・モノマーなど紫外線、電子線その他放射線照射により硬化する樹脂、アクリル樹脂、ポリエステル、ポリエチレン、ポリエチレンテレフタレート、ポリプロピレン、ポリ塩化ビニル、ポリビニルアルコール、ナイロン、ポリスチレン、ポリ酢酸ビニル等の熱可塑性樹脂およびそれらの液状プレポリマーもしくはモノマー、一般に粉末成形に用いられる有機結合剤、例えばパラフィン、樟腦などを用いることができる。また樹脂としてゼラチン、ニカワ、ウルシ等天然物をを使うことができる。

【0028】また、樹脂は被処理部材の表面に均一に行きわたる必要があるので、上記樹脂は液状または半液状の未硬化のものが最も好ましい。また、流動性を高め、部材表面に均一に行きわたらせるために固体または液状の樹脂を有機溶媒もしくは水等で溶解、希釈もしくは分散して使うことができる。この場合、溶媒又は水は混合中に蒸発するので次第に粘着性が高まり、粉体の付着が起こる。しかし有機溶媒などの量が多過ぎると、粉体物質の被処理部材表面への付着が不十分となる。また、熱可塑性樹脂は加熱して流動性および粘着性を増大させて用いることができる。粉体樹脂を溶媒などに分散しないで単独で使用する場合は、樹脂の流動性が小さくなるので、粉体粒子間に均一に分散させるために粉体樹脂は粉

体物質と同等もしくはより微細であることが望ましい。これら溶媒、水などは皮膜形成中及び形成後皮膜から蒸発させられる。

【0029】さらに、被処理部材が樹脂ボンド磁石およびプラスチック部材のように樹脂を含有するときは、その樹脂の溶剤を皮膜形成混合物に添加して、樹脂を被処理部材から溶け出させて皮膜形成混合物に供給することもできる。一旦溶け出した樹脂は溶剤の蒸発などにより樹脂の粘度が高められると、被処理部材に付着して樹脂皮膜を形成する。

【0030】次に粉体物質は被処理部材上に形成される粉体皮膜の構成物質である。粉体物質としては各種金属、合金粉末およびセラミックス粉末、さらには樹脂、プラスチック、塗料粉末などであり、防食、美観付与、絶縁性付与、強度向上などの機能を有するものであれば各種粉体を使用することができる。

【0031】一例をあげれば金属粉末としては、Al, Cu, Mg, Ti, Fe, Cr, Co, Ni, Zn, Pb, Sn, Rh, Ir, Pd, Pt, Ag, Au, Mo, Wなどの粉末およびそれらを主成分とする合金粉末がある。これらの金属はすべて樹脂より強度が優れており、また水や塩水などによる変質が少ないために耐食性が優れている。ステンレス, Cr, Ni, Mo, Wなどは表面に強固な不働態膜を作るので、耐食性に優れている。よってこれらの金属は皮膜の強度及び耐食性を高める。各金属が特長とするところを挙げると、Rh, Ir, Pd, Ag, Auなどは良好な美観と耐食性を有するので、これらの性質を皮膜に付与する。また、Cuなどは良好な耐食性と電気伝導性を有するので、耐食皮膜の形成、めっき下地皮膜の形成などに良好に使用される。Niもめっき下地皮膜の形成などに良好に使用される。Zn, Snはほとんどすべての金属を犠牲陽極効果により防食する。

【0032】セラミックス粉末は金属よりも化学的に安定であり、上記した樹脂-金属複合皮膜よりも耐食性が優れている。これらセラミックとしては例えば酸化物、 MgO , Al_2O_3 , SiO_2 , TiO_2 , CrO_2 , MnO_2 , Fe_2O_3 , FeO , Fe_3O_4 , CoO , NiO , CuO , ZnO , ZrO_2 , MoO およびそれらをベースとする複合酸化物、 TiN , BN 等各種安定な窒化物等、 SiC , WC , TiC 等各種安定な炭化物等を用いることができる。

【0033】上記した金属、セラミックスなどは樹脂に配合剤、顔料などとして含まれていてもよい。また複数種の粉末を混合して用いてもよい。

【0034】粉体物質として樹脂粉末を使用する場合は、各種熱硬化性樹脂、熱加塑性樹脂及びこれらに各種顔料を分散させた粉末樹脂を使用することができる。したがって、粉末樹脂の皮膜は完全硬化させた状態において、皮膜性と密着性が良好で結果として耐食性に優れて

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いるので、本発明においては例えば液状の樹脂と粉末樹脂を他の皮膜形成混合物と共に混練することがある。

【0035】粉体物質の粒度は、被処理部材の大きさ、皮膜の厚さ及び粉体物質の材質により変わる。セラミックス粉体など硬質で変形しにくい粉体の場合は粒度が小さいことが望ましく、延性に富む金属粉などの場合はこれより大きくてよいが一般には $0.05 \sim 500 \mu\text{m}$ の範囲内である。望ましくは $0.1 \sim 300 \mu\text{m}$ 、より望ましくは $0.1 \sim 100 \mu\text{m}$ の範囲内である。一般に、粉体は粒度が小さいほど樹脂により捕捉されやすい。また粒度が小さい粒子は、樹脂皮膜上に分散している粉体物質の粒子の間に打撃により押し込まれ易く、塑性変形による粉体同志あるいは被処理材料との圧着や結合が起こり易い。したがって粉体物質の粒度が小さいほど、打撃力が小さくて済み、また皮膜の表面粗さも小さくなる。

【0036】皮膜形成媒体は鉄、炭素鋼、その他合金鋼、銅および銅合金、アルミおよびアルミニウム合金、その他各種金属、合金製、あるいは Al_2O_3 、 SiO_2 、 TiO_2 、 ZrO_2 、 SiC 等のセラミックス製、ガラスさらに硬質プラスチック等を用いることができる。また皮膜成形に十分な打撃力が加えられるのであれば、硬質のゴムも使用することができる。これら媒体のサイズ、材質は部材の形状およびサイズ、使用する粉体の材質に応じて適宜選択する必要がある。また複数のサイズ及び材質の媒体を混合して使用することもできる。また場合によっては表面処理、表面被覆を施して使うこともできる。また複数の上記材料によって構成された複合媒体を用いてもよい。また、打撃力の緩和および平均化を行い、皮膜の均質性、膜厚のばらつきを抑えるため、木粉や軟質ゴム、軟質プラスチック等軟質の媒体を前記媒体に対し体積比の50%以下の範囲で適宜混合することがある。これらは単独では打撃力をほとんど生じないので、必ず前記皮膜形成媒体と併用される。

【0037】皮膜形成媒体の形状は、球状、楕円形、立方体、三角柱、円柱、円錐、三角錐、四角錐、菱面体、不定形体、その他各種形状を使用することができる。

【0038】皮膜形成混合物の各成分（要素）の割合は各成分の所望の作用を発揮するように、いずれかの要素に偏らず全体がバランスするように定める。粉体および樹脂の量は、部材に付与する皮膜の厚みと、部材の表面積の合計によって定まる。ただし、樹脂と粉体の比率は、樹脂の硬化後の体積に換算して樹脂分を0.5%以上に設定することが望ましい。これ以下であると、粉体の部材への付着が不充分となる。また、媒体と部材の混合比率は、部材の形状によって異なるが、少なくとも見掛け容積比で媒体を20%以上配合しないと、部材表面への均一かつ十分な打撃が行われず良好な皮膜を得ることが難しい。

【0039】容器内での振動又は攪拌は以下述べるよう

な種々の方法で実施することができる。容器2内に設けられ回転軸4に固着されたアーム3（図1参照）、回転軸4に固着された羽根5（図2参照）、または図示されてはいないインペラ、ブレードなどの攪拌機により為される。なお、図中10は皮膜形成混合物である。また、図3に示すようにドラム又はポット状容器自体をローラー6上で回転してもよい。さらに図4に示すように、回転軸に固着されたドラム状容器2を回転してもよい。容器は上部が解放されていても、また密閉されていてもどちらでもよい。加えて図5に示すように容器2を揺すってもよい。揺動中に攪拌を行ってもよい。また図6に示す回転軸4に対称的に固着されたアーム7の先端に取りつけられた容器2内に粉末混合物10を入れて遠心力で粉末混合物を混合してもよい。容器2を自転させることが好ましい。容器の動作が同じであれば、回転の機構はこれに限らず、例えばディスク状のホルダーを使ってもよい。

【0040】あるいは容器2内又は容器外に設けられた加振器8により皮膜形成混合物に振動を加えてもよい（図7参照）。以下振動を加える方法に例を取って皮膜形成混合物に加える力（加振力）の大きさを説明する。加振力を容器及び皮膜形成混合物の重力（以下「振動重力」という）で平均した値（以下、「被加振力」—無次元数—という）が皮膜形成媒体が被処理部材に加える衝撃力の指標になる。具体例として、2.8リットルの容器の重量—1kgf、スチールボール（皮膜形成媒体）の重量—10kgf、被処理部材の重量—1kgfである場合は、振動重力は12kgfとなる。このとき40Hz周期の好ましい加振力は20～50kgfである。したがって被加振力は $1.67 (= 20 / 12) \sim 4.17 (50 / 12)$ となる。

【0041】より大きい容器を使用する場合、具体例として20リットルの容器の重量—4.5kgf、スチールボール（皮膜形成媒体）の重量—70kgf、被処理部材の重量—5.5kgfである場合は、振動重力は80kgfとなる。このとき25Hz周期の好ましい加振力は150kgfである。したがって被加振力は $1.50 / 80 = 1.88$ である。

【0042】被処理部材が鉄鋼材料等の強靱な材質でできている場合は被加振力の上限は約10でもよいが、希土類磁石、ボンド磁石、セラミックス、ガラスなどの脆い材質では被加振力の上限を5以下にすることが好ましい。また、被加振力の下限は1以上、特に1.5以上であることが好ましい。被加振力がこの下限より小さいと皮膜成長速度が遅くなり、一方上限より大きいと被処理部材が脆い材質の場合その破壊が起こりやすくなり、また皮膜形成媒体の変形も起こりやすくなる。振動の周波数は特に限定されないが、2Hz～200Hzの範囲であることが好ましい。この時の振幅が0.5～10mmで上記被加振力の範囲に入る。

【0043】続いて、攪拌方式の場合は、回転により発生する遠心力が皮膜形成混合物と容器の合計重量に対して上記被加振力の範囲に入っていることが望ましい。しかし回転数が大き過ぎかつ／または容器中における皮膜形成混合物の体積割合が大きすぎると、皮膜形成混合物が容器壁に押し付けられて混合が十分に起こらない。したがって回転数は60rpm以下かつ／又は前記の体積割合は80%以下の条件を満たすことが好ましい。

【0044】さらに加振方式としては図8に示す装置を使用することができる。好ましくは1〜20°の傾斜をつけたU字状とい20の下面に加振機8を取り付け、皮膜形成混合物10に振動を加えながらとい20上を滑り落とす。断面形状はU字形には限定されず、円形、V字形、角形など各種形状のものをを用いることができる。また、とい20の上部は必ずしも解放されていなくともよい。とい20の下端の下方には振動ふるい22を設置する。振動ふるい22は被処理部材23より小さく、スチールボールなどの皮膜形成媒体24より大きいメッシュをフレームなどに固定し、全体を傾斜させるとともに加振機に連結したものである。したがって振動ふるい22上に落下した皮膜形成混合物は皮膜形成媒体24とともにメッシュを通り抜けて下方に落下し、一方被処理部材23は振動ふるい22上で搬送される。皮膜形成媒体24は振動ふるい22の下方に設けた媒体回収コンベヤー30により回収され、皮膜形成使用に再使用される。また、被処理部材23は振動ふるい22の下側端に設けた製品回収コンベヤー31により回収される。以上のような装置を使用すると、皮膜形成の連続全自動化が可能になる。さらに、とい20を図7に示すようにつづら折れまたはらせん状にして、とい20の占有面積を少なくすることができる。このつづら折れとい20の出口20aを皮膜形成混合物20bの装入部20bの真下にもつてくると、皮膜形成媒体をリターンするときのリターンパスを短くすることができる。また、図示はしていないがといを容器内に収容して容器ごと振動させることも出来る。

【0045】皮膜形成混合物の各成分の容器への装入順序としては、容器内で皮膜形成媒体を振動または攪拌によって混合し、これらの媒体を混合中の容器に被処理部材、粉体物質及び樹脂を逐次あるいは同時に挿入することが好ましい（請求項2の方法）。この方法によると均一混合程度が高められる。ここで皮膜形成媒体はあらかじめ容器内へ投じ、振動又は攪拌を加えておくことにより皮膜形成に必要な樹脂の付着をもたらし、また打撃力を発生できるが、その他の被処理部材、粉体物質及び樹脂の装入順序、回数、単独装入か同時装入かなどは全く任意である。同時装入の方法として顔料を含む樹脂を装入すると、粉体物質と樹脂が容器に同時装入となる。

【0046】ただし、特殊な装入順序が好ましい場合がある。①液状樹脂又は溶媒さらには溶媒に溶かした樹脂

と樹脂粉体（粉体物質）を使用する場合：あらかじめ、これらと樹脂粉体だけを混合してしまうと、樹脂粉体が液状樹脂に溶解しやすい場合には粉末の凝集が起こりやすく、均一な皮膜が得られない。したがって粉末状樹脂は遅い工程で容器に装入するか、あるいは容器に先に装入するときは後から装入する液状樹脂は被処理部材と同時に挿入する。②皮膜形成混合物の成分のいずれかを加熱する場合：被処理部材を加熱し容器に装入した後に樹脂を装入する；樹脂を装入した後加熱した被処理部材を装入する；加熱された被処理部材及び加熱された皮膜形成媒体を容器に装入した後に樹脂を装入する。

【0047】樹脂を振動又は攪拌中に硬化させることによって、樹脂皮膜に捕捉された粉体物質の固定力を高めることができる（請求項3の方法）。樹脂の硬化の方法としては、二液混合型常温硬化タイプを使用して硬化剤により硬化させる、加熱硬化型樹脂を加熱により硬化させる、溶媒を蒸発させる、さらには紫外線、γ線、電子線やその他の放射線照射により硬化させるなどの方法が可能である。

【0048】さらに、粉体物質以外の皮膜形成混合物をあらかじめ容器内にて混合し、粉体物質を後から容器内に装入することができる（請求項4の方法）。この方法による利点は以下の①〜③とおりである。

【0049】①特に溶媒で希釈したような流動性が大きい樹脂を被処理部材表面に十分に均等に行き渡らせることにより十分に均等な樹脂皮膜を作り、粉体物質で均一に被覆することができる。

【0050】②下地となる被処理部材との界面近傍の皮膜は樹脂がrichになり、皮膜の表面は粉体物質がrichになり、皮膜内ではこれらの成分の割合が連続的に変化する遷移層が存在する。そのため皮膜の密着力が高い。

【0051】③皮膜の表面付近では粉体物質が圧入され、粉体物質の割合が70〜90体積%場合によってはほとんど100%と極めて高く、樹脂塗膜の顔料配合率を遥かに超える。したがって、粉体物質が塗料の顔料として使用されるTiO₂、MgO、Fe₂O₃などである場合は被覆表面は水、その他の腐食成分を遮断する性能が非常に良好になる。通常樹脂塗装では重防食のために塗膜を多層塗りして顔料の量を多くしているが、これは手間がかかり、層間剥離を起こしやすく、また膜厚が大きくなる問題がある。本発明法では1回の処理で顔料が多い皮膜を得ることができ、また膜厚が薄いという利点がある。

【0052】本発明においては、樹脂皮膜をあらかじめ被処理部材に形成しておき、その後被処理部材、皮膜形成媒体及び粉体物質の振動又は攪拌させることができる。したがってかかる本発明の別法は、被処理部材表面に皮膜を形成する方法において、皮膜形成過程の少なくとも初期において少なくとも部分的に未硬化状態にある

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第一の樹脂皮膜を施した被処理部材、粉体物質（皮膜形成過程において前記樹脂よりも硬質の樹脂粉末のことがある）、及び前記被処理部材よりは寸法が実質的に大きくかつ前記粉体物質よりは寸法が実質的に小さい皮膜形成媒体に容器内にて振動又は攪拌を加えることを特徴とする皮膜形成方法である（請求項 5）。

【 0 0 5 3 】 この樹脂皮膜は請求項 1 において外部から被処理部材に付着させた樹脂皮膜と同様に作用して粉体物質を捕捉する。被処理部材が樹脂ボンド磁石あるいはプラスチック部材のようである場合は、これを溶媒に浸漬して引上げると磁石の表面付近の樹脂が溶けだして樹脂皮膜を簡単に作ることができる。

【 0 0 5 4 】 さらに、本発明の別法を実施する際に樹脂皮膜に粉体物質をまぶし（すなわち、樹脂皮膜がもっている付着力を利用して粉体物質を接着させる）、その後上記別法を実施することができる。

【 0 0 5 5 】 本発明の別法を実施する際に、前記樹脂（第一の樹脂）と同種又は異種の樹脂（第二の樹脂）を皮膜形成混合物に添加することができる（請求項 6 の方法）。第二の樹脂は既に形成されている樹脂皮膜上に流動して、層を作り、成長し、粉体物質—樹脂間の結合をもたらす。かかる第二の樹脂としては請求項 2 に関して前述した樹脂を使用することができる。

【 0 0 5 6 】 本発明における混合後に、皮膜を形成した被処理部材の皮膜の樹脂を硬化することにより、皮膜を強化させた密着性を向上することができる（請求項 7 の方法）。硬化は皮膜を混合容器内であるいは容器外で樹脂の重合温度に加熱する、常温に放置して溶剤を蒸発させるなどにより行う。この硬化処理は皮膜強度、密着性などが不充分である場合、形成された皮膜を下地として更にその上に本発明の皮膜を形成し、多層皮膜を得る場合にも有効である。さらに樹脂の種類によっては紫外線あるいはガンマ線、電子線等により硬化することもできる。

【 0 0 5 7 】 皮膜形成直後にはその上に未固定の粉体が多く残留していることがあり、これらの粉体は埃や塵を嫌う電気、電子部品あるいは精密機械部品等に本発明により処理された部材を使用する場合には除去する必要がある。したがって、超音波洗浄、空気の吹き付けなどの方法により遊離粉体を除去することが好ましい（請求項 8 の方法）。遊離粉体の除去は樹脂の硬化前又は後のいずれでも実施することができる。

【 0 0 5 8 】 遊離粉体の除去においては皮膜表面を軟質の媒体で摩擦することも可能である（請求項 9 の方法）。このためには軟質の媒体と皮膜を形成した部材を容器内にて混合する、例えば容器に振動を加える、軟質媒体と部材を攪拌することができる。この方法では軟質の媒体と残留粉末の間の剪断力によって残留粉末が除去され、加えて皮膜の表面が磨かれる。この方法は超音波洗浄よりも残留粉末の除去効果が大きく、また美しい外

観が得られる。したがって装飾用品、外装用品に本発明の部材を使用する場合に好適である。

【 0 0 5 9 】 上記した軟質の媒体としては、それ自身が衝撃吸収力のある程度有しているので、被処理部材に強い打撃力を与えて形成された皮膜を疵つけたり、深く削り取ったりしないものが好ましい。例えば、木屑、木材粉、クルミ殻、軟質プラスチック、ゴムなどが望ましい。さらに木屑などに油分などをしみ込ませて表面研磨の効果あるいは防錆性を高めることもできる。

【 0 0 6 0 】 また、本発明に係る皮膜形成後の被処理部材に熱処理を施すことができる（請求項 10 の方法）。この目的の一つは樹脂の硬化である。樹脂の硬化温度は樹脂の種類により異なるが一般に 30 ~ 200℃であり、また硬化時間は 1 ~ 500 分程度である。かかる温度及び時間の熱処理を行うことにより樹脂を硬化させることができる。

【 0 0 6 1 】 熱処理の他の目的は、粉体物質の粒子同士あるいは粉体物質と被処理部材の間の結合力を熱拡散により増大することである。さらには皮膜のピンホールを減少させできるだけ連続した膜とすることである。また、多層膜の各層間の拡散による膜質の均質化、および耐食性や機械的性質の向上を意図することもある。

【 0 0 6 2 】 熱処理の温度は粉体物質の融点（ M_p : K）以下で（ $1/3$ ） M_p 以上が好ましい。熱処理温度が粉体物質の融点を超えると粉体物質が溶けて、湯だれや部材同士の溶着を起こす。熱処理温度が融点の $1/3$ より低いと目的とする効果が得られ難い。この熱処理温度は当然に被処理部材の融点よりは低くなければならないから、熱処理温度より融点が高い物質からなる被処理部材に本方法は適用される。また、熱処理温度は樹脂の分解温度よりも通常は高くなるから、熱処理後は皮膜はほとんど粉体物質から構成される。本方法を適用する場合は樹脂は比較的低温で容易に分解蒸発し、皮膜に炭素などを残留させないもの、例えばパラフィン、ポリプロピレン、各種ワックスなどが好ましい。また樹脂は熱処理前で皮膜中の含有割合ができるだけ少ないことが望ましい。その割合は例えば 50 % 以下である。

【 0 0 6 3 】 上記した熱処理は、粉体物質が Zn 、 Sn またはこれらの合金のように比較的低融点である時に有効である。すなわちこれらの Zn などはほとんどすべての金属を犠牲防食効果により防食できるが、そのためには皮膜構造が連続膜に近いことが必要である。本発明方法により得られる粉体物質が分散した皮膜では雨水、塩水に絶えずさらされるような過酷な腐食環境において犠牲防食効果が十分には発揮されないが、熱処理によって、十分に良好な耐食性を付与する犠牲防食効果が得られる。従来 Zn 、 Sn の皮膜は電気めっきあるいは溶融めっきにより形成されてきたが、前者は湿式プロセスであるために廃水や副産物処理の問題があり、後者はめっき厚さが 100 μm 以上と厚く、薄い皮膜が得られずま

た小物部品には適さないという問題があった。これに対して本発明法は簡便なドライプロセスにより小物部品に薄い皮膜を形成することができるから、電気めっきあるいは溶融めっきでは問題を伴う耐食性皮膜形成の分野に好適である。

【0064】さらに、粉体物質がAl, Snなどの耐食性が高い物質である場合は熱処理を大気中で実施することができるが、真空中あるいは不活性ガス中で熱処理を行うことが好ましい。

【0065】続いて請求項11の方法は、上記した皮膜の表面に樹脂の保護皮膜を施す方法である。この方法は熱処理を施さない皮膜に適用される場合は皮膜の強度及び耐食性を向上させる効果がある。皮膜の表面は樹脂分が少なく、また残留粉体を除去したとしても、なお粉末の固定力が弱い。本発明部材は摺動部材としての使用を意図していないので、絶えず外部から皮膜に力が掛かることはないが、取扱中や部材を機械に取り付け中に外部から衝撃力や強い力が掛かると、粉体物質が脱落したりあるいは皮膜が局部的に破壊されることがある。このような不都合を防止するために樹脂の皮膜を施すことは有効である。樹脂の皮膜は表面を滑らかにし美観も向上させ、さらにピンホールを埋め水分の浸透を妨げる。

【0066】熱処理を施した皮膜に樹脂被覆を適用すると、熱処理温度が高くとも、ピンホール等の完全除去が困難な場合、あるいは熱処理中に気泡や亀裂が生ずるような場合、これを封孔、封止する。

【0067】樹脂被覆形成の方法はスプレーあるいは被処理部材を樹脂中に浸漬させても良いが、請求項12記載の方法のように樹脂皮膜形成媒体を使用すると薄くかつ均一に皮膜を形成することができる。樹脂皮膜形成媒体は本発明の第一の皮膜形成媒体の原理を樹脂被覆形成に応用したものである。

【0068】さらに樹脂被覆を顔料を含有した通常の塗料の塗装により行うこともできる（請求項13記載の方法）。この場合は上述した樹脂被覆の効果に加えて、良好な美観を得ることができる。

【0069】また保護皮膜としては樹脂皮膜の他に金属又は合金のめっきあるいは金属と非金属の分散めっき（電気めっきあるいは電解めっき）を施すことができる（請求項14の方法）。従来下地がセラミックス、プラスチックなどの非導電性物質であるかあるいは樹脂ボンド磁石のように導電性が悪く不均一な物質であると、直接電気めっきを行うことは困難であり、また可能であるとしても複雑な前処理が必要であった。したがって、下地に無電解めっきを行ってから電気めっきを行うコストと手間がかかる方法が一般に行われていた。これに対して本発明は下地に金属richな層を強固にしかも容易に付与することができるので、非導電性物質の電気めっきが極めて簡単になる。

【0070】また従来めっきが可能な物質であっても、

めっき合金や金属-非金属複合めっきの組成を広い範囲で調節することは困難であった。これに対して本発明は非電気化学的方法により皮膜を形成するので組成調節の範囲が極めて広い。

【0071】また、従来めっき電解液と被処理部材の化学反応によりめっきが困難であるか不可能な場合があった。本発明は係る場合にも容易にめっきを可能にするものである。その一例として粉末冶金材料へのめっきがある。これはポアを有するのでめっき電解液と接触させると内部にまでめっき液が浸透し、内部の腐食や非所望の内部に電着が起こる。これを避けるためにはPVDなどで金属皮膜を形成した上にめっきを行えばよいが、PVDは大掛かりな装置を必要とする。これに対して本発明法によると極めて簡単な方法によりめっきの下地を作ることができる。AgやMgなど活性な軽金属あるいはそれらの合金等はめっき液への部材の溶け出しが起こり、ジンケート処理など特殊な前処理を行わなければめっきが不可能であったが、本発明法によれば簡単な方法によりこうした部材へのめっきも可能にする。

【0072】めっき皮膜の下地となる本発明の粉体物質皮膜は粉体物質の粒子の間隙などに多少のピンホールが形成されるので、めっき皮膜にもピンホールが形成されることがある。この場合めっき皮膜を若干厚くするか、あるいはめっき皮膜の下地に無電解めっき皮膜を極薄く形成することにより、めっき皮膜でのピンホールを防止することができる。

【0073】請求項16、17は本発明方法による皮膜の適用が極めて有利な被処理部材に関する。その利点を説明する前に希土類磁石及びその保護皮膜につき従来技術を説明する。

【0074】希土類永久磁石はその優れた磁気特性ゆえに、需要は増加の一途をたどっている。現在生産されているほとんどの希土類永久磁石はSmとCoを主成分とするSm-Co系と、Nd-Fe-B系であり、また製造法としては焼結によるものと樹脂により結合した樹脂ボンド磁石がほとんどである。樹脂ボンド磁石は、磁石粉末と樹脂を混合した後圧縮成形を行い、その後樹脂を硬化する方法、射出成形法、磁石粉末をプレスした後に樹脂を含浸させる方法などにより製造されている。希土類磁石は活性な希土類元素を多量に含んでいるために、高温多湿な環境で使用されると腐食による性能劣化や性能のばらつきを生じ、また腐食生成物質が汚染源となる。特にNd-Fe-B磁石は鉄を主成分とするために、耐食性が低く、防食皮膜の付与が不可欠であり、現在、Niめっきが焼結磁石に、エポキシ樹脂などの吹付けや電着塗装が焼結及び樹脂ボンド磁石に対して行われている。しかしながら小物部品が多いNd-Fe-B焼結磁石に施すNiめっきは、めっき法に関して既に説明したようにめっき操作が厄介、廃液処理などの問題がある他に、下地の酸化物の除去が不十分であるとめっきの

密着性が劣るという問題もある。樹脂の塗装も既に説明したように塗装操作に手間がかかる等の問題がある。

【0075】またボンド磁石は価格が安いために樹脂の多層塗装は現実的でないために、単層塗装が主流になっている。このために樹脂ボンド磁石の耐食性は焼結磁石よりは低いレベルに留まっている。この欠点解消の対策として、無電解めっき下地の上に電気めっきを施すことが提案されている（特開平 3 - 1 1 6 7 0 3 号）が、上述したような問題がある。電着塗装を使用すればスプレー塗装より耐食性は若干向上するが、これは大掛かりな塗装および廃液処理設備も必要であり、基本的には治具に釣り下げて行うためコスト高となる。さらに樹脂ボンド磁石は焼結製品よりも一層多孔質であるので無電解めっきを相当に厚くしなければ、良好な下地とならない。また $Nd - Fe - B$ 系を被処理部材とする無電解めっき液は浴組成の管理が非常に難しいと言われている。

【0076】本発明により希土類磁石表面に形成される粉体-樹脂分散皮膜は以下のような利点をもっている。

①焼結磁石の場合：従来のめっき皮膜に対しては、下地処理が特に必要とされない；皮膜形成条件が緩やかである（すなわち、特に $Nd - Fe - B$ 磁石を念頭に置いて条件を設定する必要がない）。従来の樹脂皮膜に対しては、安定な酸化物、例えば TiO_2 、 MgO 、 Fe_2O_3 などの粉体を皮膜中に分散させ、特に皮膜表面でその含有量を多くすることにより、耐食性を良好にすることができる。

【0077】図 1 2 に TiO_2 粉体とエポキシ樹脂を使用した実施例 1 中の 3 の方法により得られた皮膜の断面構造を電子顕微鏡写真（SEM 像、倍率 10000 倍）で調査した結果を示す。図中、皮膜全体で粒子状に見えるものが TiO_2 である。皮膜の上部、下部、これらの中間に連続相状に見えるのがエポキシ樹脂である。また皮膜の左下側に見える輪郭が不鮮明な粒子は樹脂と TiO_2 が混合していることを示している。 TiO_2 粒子の間に介在している樹脂は（ ）では明瞭に認められるが、写真では明瞭ではない。図 1 2 から分かるように、本発明方法により作られた皮膜は粉体が極めて密に集まっている。

【0078】②樹脂ボンド磁石の場合：従来の樹脂塗装に対しては、多層膜並の耐食性が得られるので、従来の単層樹脂皮膜よりも耐食性が大幅に向上する；特に、請求項 6、7 のように最初に樹脂皮膜を形成すると、樹脂ボンド磁石の孔に粉体物質や樹脂が圧入されるために、封孔効果が大きく、このために耐食性が向上する。従来の無電解めっき-電解めっきに対しては、導電性粉体物質を使用する本発明皮膜は工業的応用可能性が非常に高い。

【0079】本発明により希土類磁石表面に形成された粉体-樹脂分散皮膜上にめっき皮膜を形成すると以下のような利点がある。

①焼結磁石の場合（従来のめっき皮膜と比較して）母材表面上に本発明法によるめっき下地層が樹脂により強固に密着しているため、めっき下地層をその上に形成されるめっき層に対し適切に選ぶことにより、密着性の優れためっき皮膜が得られる。まためっき皮膜は通常若干のピンホールを有するが、これらピンホールは従来のめっき皮膜であると、直接母材表面に達しているためピンホールから侵入した腐食成分はめっき層と母材表面の界面に浸透し、膜はがれ等を起こしやすかった。特に母材表面に酸化層が残留している場合は極めて膜はがれを起こしやすい。ところが本発明法では、めっき皮膜の下に防食性のよい樹脂、粉体混合皮膜が存在するため、ピンホールからの腐食成分はほとんどすべてこの下地層によって止められ、母材表面に拡散しないため、膜はがれはなくなる。

【0080】②樹脂ボンド磁石の場合（従来の無電解めっきと比較して）：無電解めっきは、一般に浴が高価で廃液処理等に多額の費用がかかるため、コスト高となる。また、下地との密着力は樹脂皮膜よりは数段劣る。また一般に無電解めっきは厚膜化が難しく $5 \mu m$ 以下の薄膜にとどめられており、特にボンド磁石は多孔質体なので、母材表面のピンホールを拾って極めてポーラスな皮膜となる。このような膜はその上に形成される電解めっき膜のピンホールから浸透してくる腐食成分の遮断能力がほとんどなく、膜はがれ等のばらつきを生じやすい。また無電解めっきのめっき液がボンド磁石のピンホールに残留しやすく、これも膜はがれの大きな原因となる。これらの問題点のため、無電解めっきを付与した Nd 系ボンド磁石は未だ量産に至っていない。

【0081】本発明法によれば、磁石表面のピンホールが樹脂によって封止され、さらにこの樹脂層によりめっきの下地となる金属層が強固に密着されるため、その上に形成されるめっき皮膜も良好な密着性を持つ。この下地層は①と同様、磁石表面への腐食成分の拡散を防止するため、結果として従来法よりはるかに優れた耐食性が得られる。

【0082】以上説明した方法では樹脂により皮膜を形成する方法を説明したが、無機系の粘着物質、例えば水ガラスに代表されるケイ酸塩などは粉体物質、皮膜形成媒体及び被処理部材を一様に分散させかつ混合させることができ、また温度、溶媒又は水希釈などにより粘度を混合中に低下させることによってガラス皮膜を被処理部材表面に形成することができる。またガラス皮膜は粉体物質を捕捉することができる。したがって樹脂に代えてあるいは樹脂と共に無機粘着物質を使用することができる。

【0083】以下、実施例により本発明を詳しく説明する。

【実施例】

50 実施例 1

$\text{Fe}_{81}\text{Nd}_{13}\text{B}_6$ の組成をもつ粒度 $100\mu\text{m}$ 以下の急冷ポンド磁石用粉末を使用した。この粉末にエポキシ樹脂を $3\text{wt}\%$ 加えて混合し、 $5\text{ton}/\text{cm}^2$ の加圧力で圧縮成形して、 $22\text{mm}\phi \times 20\text{mm}\phi \times 10\text{mm}$ の成形体を 220 個得た。これを 150°C で 1 時間キュアーし、樹脂結合磁石とした。次に容積 2.8 リットル、深さ 150mm の円形のポットに、直径 $\phi 3.0\text{mm}$ の鋼球を 10kg (見掛け密度 $5\text{kg}/\text{リットル}$) 投入し、振動数 2500c.p.m. (cycle per minute)、振幅 5mm の振動を加えながら、平均粒度 $1\mu\text{m}$ の Al 粉末を 20g 投入し 5 分間 Al 粉に振動を加えた。

【0084】次にあらかじめエポキシ樹脂 10% (樹脂 97% 、硬化剤 3%) を溶かしたメチルエチルケトン (MEK) に浸漬して表面を樹脂で覆った磁石を 20 個投入し、 15 分間振動させた後取り出した。 120°C で 2hr 加熱し最後に平均粒径 2mm のクルミ殻片 2.0kg と共に同じサイズのポットに入れて 5 分間振動させ、表面に残留した余剰の粉末を除去した。以上の方法で平均膜厚 $10\mu\text{m}$ (最大値 $5\mu\text{m}$ 、最小値 $2\mu\text{m}$) の皮膜を形成した磁石を $85^\circ\text{C} \times 90\%\text{RH}$ の条件で耐食性を評価した。その結果を表 1 に「1」として示す。

【0085】以下同様の方法により但し下記の条件を変更して粉末を被覆した磁石 ($2 \sim 11$) をそれぞれ 20 個ずつ作成した。

2- Al 粉末に代えて、平均粒径が $1\mu\text{m}$ の Cu 粉末を使用した。

3- Al 粉末に代えて、平均粒径が $0.3\mu\text{m}$ の TiO_2 粉末を使用した。

4- Al 粉末に代えて、平均粒径が $1\mu\text{m}$ の Al_2O_3 粉末を使用した。

5- Al 粉末に代えて、平均粒径が $2\mu\text{m}$ の MgO 粉末を使用した。

6- Al 粉末に代えて、平均粒径が $2\mu\text{m}$ の Fe_2O_3 粉末を使用した。

7- Al 粉末に代えて、平均粒径が $2\mu\text{m}$ の Fe_2O_3 粉末を使用した。

8- Al 粉末に代えて、平均粒径が $1\mu\text{m}$ の Cu 粉末を使用して膜厚が $5\mu\text{m}$ の皮膜を形成した後、電解めっきにより $10\mu\text{m}$ の膜厚の Ni めっき層を形成した。

9-樹脂結合磁石に、 TiO_2 添加量が 20% のエポキシ樹脂をスプレー塗装し、 120°C で 6 時間キュアーして、平均 $10\mu\text{m}$ の膜厚の塗膜 (単膜) を形成した (比較例)。

10-樹脂結合磁石に、リン酸亜鉛化成処理液をスプレー吹き付けし、乾燥後、 TiO_2 添加量が 20% のエポキシ樹脂をスプレー塗装し、 120°C で 6 時間キュアーして、 $10\mu\text{m}$ の膜厚の塗膜 (単膜) を形成した (比較例)。

11-樹脂結合磁石に皮膜を施さず、そのまま試験した (比較例)。

以上のようにして各種皮膜を形成した樹脂結合磁石を各 20 個湿潤試験して、耐食性を評価した。試験条件: $85^\circ\text{C} \times 90\%\text{RH}$ 放置 (チェック項目: 外観) 結果を次表に示す。

【0086】

【表 1】

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	B	C	D
2	A	B	B	C
3	A	A	B	B
4	A	A	B	C
5	A	A	B	B
6	A	A	B	B
7	A	A	A	B
8	A	A	A	A
9	B	C	E	—
10	A	B	D	—
11	D	E	—	—

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の 1 0 %未満に顕微鏡オーダーの点錆

C 全体の 1 0 %未満に目視でわかる点錆

D 全体の 1 0 %以上 3 0 %未満にやや大きな発錆

E 全体の 3 0 %以上に著しい発錆、膜ふくれ、はがれ

【 0 0 8 7 】実施例 2

SmCo₅ の組成を持つ平均粒度 2 0 μ m のボンド磁石粉末を使用した。この粉末にエポキシ樹脂を 3 w t % 加えて混合し、5 t / c m² の加圧力で圧縮成形して、2 2 m m φ × 2 0 m m φ × 1 0 m m の成形体を 8 0 個得た。これを 1 5 0 °C で 1 時間キュアし樹脂結合磁石とした。次に容積 2 . 8 リットル深さ 1 5 0 m m の円形ポットに、直径 φ 3 . 0 m m の鋼球を 1 0 k g 投入し、振動数 2 5 0 0 c . p . m . 、振幅 5 m m の振動を加えながら、平均粒度 1 μ m の Al 粉末を 2 0 g 投入し、5 分間 Al 粉末と鋼球に振動を加えた。次にあらかじめエポキシ樹脂 (1 0 % M E K 溶液) に浸漬して表面を樹脂で覆った磁石を 2 0 個投入し、1 5 分間振動させた後取り出した。磁石を 1 2 0 °C で 2 h r 加熱してエポキシ樹脂

をキュアした後最後に平均粒径 2 m m のクルミ殻 2 k g と共に、皮膜形成用と同じサイズのポットに入れて 5 分間振動させ、表面に残留した余剰の粉末を除去した。

【 0 0 8 8 】以下同様の方法により各種粉末を被覆した磁石をそれぞれ 2 0 個ずつ作成し、8 5 °C × 9 0 % R H の条件で耐食性を評価した (チェック項目 - 外観) 。その結果を表 2 に示す。表中、左欄の数字はそれぞれ以下の処理を意味する。

1 - 上記の処理により平均膜厚が 1 0 μ m の皮膜を形成
2 - Al 粉末に代えて、平均粒径が 0 . 3 μ m の T i O₂ 粉末を使用した。

3 - 樹脂結合磁石に、T i O₂ 添加量が 2 0 % のエポキシ樹脂をスプレー塗装し、1 2 0 °C で 6 時間キュアして、1 0 μ m の膜厚の塗膜 (単膜) を形成した (比較例) 。

4 - 樹脂結合磁石に皮膜を施さず、そのまま試験した (比較例) 。

【 0 0 8 9 】

【表 2】

30

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	250hr	500hr	1000hr	1500hr
1	A	A	A	B
2	A	A	A	A
3	A	A	B	B
4	C	C	D	E

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の10%未満に顕微鏡オーダーの点錆

C 全体の10%未満に目視でわかる点錆

D 全体の10%以上30%未満にやや大きな発錆

E 全体の30%以上に著しい発錆、膜ふくれ、はがれ

【0090】実施例3

Sm(Co_{0.72}Fe_{0.2}Cu_{0.06}Zr_{0.03})_{8.3}の組成を持つ粒度100μm以下のボンド磁石用粉末を使用し、この粉末にエポキシ樹脂を3wt%を加えて混合し、5t/cm²の加圧力で圧縮成形して、22mmφ×20mmφ×10mmの成形体を100個得た。これを150℃で1時間キュアし樹脂結合磁石とした。次に容積2.8リットル深さ150mmの円形ポットに、直径φ3.0mmの鋼球を10kg投入し、振動数2500c.p.m.、振幅5mmの振動を加えながら、平均粒度1μmのCu粉末を20g投入し5分間Cu粉末と鋼球に振動を加えた。次にあらかじめエポキシ樹脂(10%MEK溶液)に浸漬して表面を樹脂で覆った磁石を20個投入し、15分間振動させた後取り出した。次に、磁石を120℃で2hr加熱してエポキシ樹脂をキュアした後、最後に平均粒径2mmのクルミ殻2kg

と共に皮膜形成用と同じサイズのポットに入れて5分間振動させ、表面に残留した余剰の粉末を除去した。以下同様の方法により各種粉末を被覆した磁石をそれぞれ20個ずつ作成し、85℃×90%RHの条件で耐食性を評価した(チェック項目-外観)。その結果を表2に示す。

【0091】表中、左欄の数字はそれぞれ以下の処理を意味する。

1-上記の処理により平均膜厚が10μmの皮膜を形成

2-Cu粉末に代えて、平均粒径が1μmのMgO粉末を使用した。

3-Cu粉末に代えて、平均粒径が1μmのFe₂O₃粉末を使用した。

4-樹脂結合磁石に、TiO₂添加量が20%のエポキシ樹脂をスプレー塗装し、120℃で6時間キュアして、10μmの膜厚の塗膜(単膜)を形成した(比較例)。

5-樹脂結合磁石に皮膜を施さず、そのまま試験した(比較例)。

【0092】

【表3】

	250hr	500hr	1000hr	1500hr
1	A	A	A	B
2	A	A	A	A
3	A	A	A	A
4	A	A	B	B
5	B	C	C	D

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の10%未満に顕微鏡オーダーの点錆

C 全体の10%未満に目視でわかる点錆

D 全体の10%以上30%未満にやや大きな発錆

E 全体の30%以上に著しい発錆、膜ふくれ、はがれ

【0093】実施例4

50 Sm₂Fe₁₇N₃の組成を持つ平均粒度2.5μmのボ

ンド磁石用粉末を使用した。この粉末にエポキシ樹脂を3wt%を加えて混合し、 5 t/cm^2 の加圧力で圧縮成形して、 $22\text{ mm}\phi \times 20\text{ mm}\phi \times 10\text{ mm}$ の成形体を80個得た。これを 150°C で1時間キュアし樹脂結合磁石とした。次に容積2.8リットル深さ150mmの円形ポットに、直径 $\phi 3.0\text{ mm}$ の鋼球を10kg投入し、振動数2500c.p.m.、振幅5mmの振動を加えながら、平均粒度 $1\text{ }\mu\text{ m}$ のAl粉末を20g投入し5分間Al粉末と鋼球に振動を加えた。次にあらかじめエポキシ樹脂(10%MEK溶液)に浸漬して表面を樹脂で覆った磁石を20個投入し、15分間振動させた後取り出した。磁石を 120°C で2hr加熱してエポキシ樹脂をキュアした後、最後に平均粒度2mmのクルミ殻0.2kgと共に皮膜形成用と同じサイズのポットに入れて5分間振動させ、表面に残留した余剰の粉末を除去した。

【0094】以下同様の方法により各種粉末を被覆した

	250hr	500hr	1000hr	1500hr
1	A	A	B	C
2	A	A	B	B
3	B	B	C	E
4	D	D	E	-

A 全数全く発錆なし

B 巨視的には発錆なし。全体の10%未満に顕微鏡オーダーの点錆

C 全体の10%未満に目視でわかる点錆

D 全体の10%以上30%未満にやや大きな発錆

E 全体の30%以上に著しい発錆、膜ふくれ、はがれ

【0097】実施例5

$\text{Nd}_{13.8}\text{Dy}_{0.4}\text{Fe}_{78.2}\text{B}_{7.6}$ の組成をもつインゴットをスタンプミルで平均粒径が $20\text{ }\mu\text{ m}$ になるように粗粉砕し、次にジェットミルで平均粒径が $3.0\text{ }\mu\text{ m}$ になるように粉砕した。この微粉砕粉に12kOeの磁場をかけながら金型中で磁場と直角の方向に 1.5 t/cm^2 の力で加圧し圧粉体を得た。この圧粉体を真空中で 1100°C で2時間焼結した後 650°C で1時間時効処理して120個の焼結体を得た。この焼結体をグラインダーで全面研磨した後、遠心バレル研磨によりコーナーを落とし、続いて洗滌乾燥した。製品の寸法は $20\text{ mm}\phi \times 5\text{ mm}$ の円盤状であった。次に容積2.8リットル深さ150mmの円形ポットに、直径 $\phi 3.0\text{ mm}$ の鋼球を10kg投入し、振動数2500c.p.m.、振幅5mmの振動を加えながら、平均粒度 $1\text{ }\mu\text{ m}$ のAl粉末を20g投入し5分間Al粉末と鋼球に振動を加えた。

磁石をそれぞれ20個ずつ作成し、 $85^\circ\text{C} \times 90\% \text{RH}$ の条件で耐食性を評価した(チェック項目-外観)。その結果を表4に示す。

【0095】表中、左欄の数字はそれぞれ以下の処理を意味する。

1-上記の処理により平均膜厚が $10\text{ }\mu\text{ m}$ の皮膜を形成
2-Al粉末に代えて、平均粒径が $0.3\text{ }\mu\text{ m}$ の TiO_2 粉末を使用した。

3-樹脂結合磁石に、 TiO_2 添加量が20%のエポキシ樹脂をスプレー塗装し、 120°C で6時間キュアして、 $10\text{ }\mu\text{ m}$ の膜厚の塗膜(単膜)を形成した(比較例)。

4-樹脂結合磁石に皮膜を施さず、そのまま試験した(比較例)。

【0096】

【表4】

次にあらかじめエポキシ樹脂(10%MEK溶液)に浸漬して表面を樹脂で覆った磁石を20個投入し、15分間振動させた後取り出した。樹脂を 120°C で2hr加熱してエポキシ樹脂をキュアした後、最後に平均粒径2mmのクルミ殻2kgと共に同じサイズのポットに入れて5分間振動させ、表面に残留した余剰の粉末を除去した。

【0098】以下同様の方法により各種粉末を被覆した磁石をそれぞれ20個ずつ作成し、 $85^\circ\text{C} \times 90\% \text{RH}$ の条件で耐食性を評価した。その結果を表5に示す。

【0099】表中、左欄の数字はそれぞれ以下の処理を意味する。

1-上記の処理により平均膜厚が $10\text{ }\mu\text{ m}$ の皮膜を形成
2-Al粉末に代えて、平均粒径が $0.3\text{ }\mu\text{ m}$ の TiO_2 粉末を使用した。

3-Al粉末に代えて、平均粒径が $0.3\text{ }\mu\text{ m}$ の TiO_2 粉末を使用して皮膜を形成した(残留粉の除去せず)後、エポキシ樹脂(5%MEK溶液)に浸漬し、再び、平均粒径が $0.3\text{ }\mu\text{ m}$ の TiO_2 粉末を使用して皮膜を形成した(残留粉の除去せず)。その後、 120°C で2時間キュアし、続いてクルミ殻による残留粉の除去を行い、平均膜厚が $20\text{ }\mu\text{ m}$ (最大値 $27\text{ }\mu\text{ m}$ 、最小値 18

μm) の皮膜を形成した。

4-A1粉末に代えて、平均粒径が $1\mu\text{m}$ の TiO_2 粉末を使用して皮膜を形成した(残留粉の除去せず)後、エポキシ樹脂(5%MEK溶液)に浸漬し、再び、平均粒径が $0.3\mu\text{m}$ の TiO_2 粉末を使用して皮膜を形成した(残留粉の除去せず)。その後さらにエポキシ樹脂(5%MEK溶液)に浸漬し、続いて 120°C で2時間キュアし、続いてクルミ殻による残留粉の除去を行い、平均膜厚が $22\mu\text{m}$ (最大値 $29\mu\text{m}$ 、最小値 $20\mu\text{m}$)の皮膜を形成した。

10 【表5】

	250hr	500hr	1000hr	1500hr
1	A	B	B	C
2	A	A	B	C
3	A	A	A	B
4	A	A	A	A
5	A	A	B	B
6	C	E	-	-
7	E	-	-	-

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の10%未満に顕微鏡オーダーの点錆

C 全体の10%未満に目視でわかる点錆

D 全体の10%以上30%未満にやや大きな発錆

E 全体の30%以上に著しい発錆、膜ふくれ、はがれ

【0101】実施例6

SmCo_5 の組成をもつインゴットをスタンプミルで平均粒径が $25\mu\text{m}$ になるように粗粉碎し、次にジェットミルで平均粒径が $4.0\mu\text{m}$ になるように粉碎した。この微粉碎粉に 12kOe の磁場をかけながら金型中で磁場と直角の方向に $1.5\text{t}/\text{cm}^2$ の力で加圧し圧粉体を得た。この圧粉体を真空中で 1210°C で2時間焼結し、その後徐冷して80個の焼結体を得た。この焼結体をグラインダーで全面研磨した後、遠心バレル研磨によりコーナーを落とし、洗滌乾燥した。製品の寸法は $20\text{mm}\phi\times 5\text{mm}$ の円盤状であった。次に容積 2.8リットル 深さ 150mm の円形ポットに、直径 $\phi 3.0\text{mm}$ の鋼球を 10kg 投入し、振動数 2500c.p.m. 、振幅 5mm の振動を加えながら、平均粒度 $0.3\mu\text{m}$ の TiO_2 粉末を 20g 投入し5分間 TiO_2 と鋼球に振動を加えた。次にあらかじめエポキシ樹脂(10

5-A1粉末に代えて、平均粒径が $1\mu\text{m}$ の Fe_2O_3 粉末を使用した。

6-樹脂結合磁石に、 TiO_2 添加量が20%のエポキシ樹脂をスプレー塗装し、 120°C で6時間キュアして、 $10\mu\text{m}$ の膜厚の塗膜(単膜)を形成した(比較例)。

7-樹脂結合磁石に皮膜を施さず、そのまま試験した(比較例)。

【0100】

【表5】

%MEK溶液)に浸漬して表面を樹脂で覆った磁石を20個投入し、15分間振動させた後取り出した。 120°C で2hr加熱後最後に平均粒径 2mm のクルミ殻 2kg と共に同じサイズのポットに入れて5分間振動させ、表面に残留した余剰の粉末を除去した。

【0102】以下同様の方法により各種粉末を被覆した磁石をそれぞれ20個ずつ作成し、 $85^\circ\text{C}\times 90\%\text{RH}$ の条件で耐食性を評価した。その結果を表6に示す。

【0103】表中、左欄の数字はそれぞれ以下の処理を意味する。

1-上記の処理により平均膜厚が $10\mu\text{m}$ の皮膜を形成

2-上記の処理を2回行い、平均膜厚が $20\mu\text{m}$ の皮膜を形成

3-焼結磁石に、 TiO_2 添加量が20%のエポキシ樹脂をスプレー塗装し、 120°C で6時間キュアして、平均 $20\mu\text{m}$ の膜厚の塗膜(単膜)を形成した(比較例)。

4-焼結磁石に皮膜を施さず、そのまま試験した(比較例)。

【0104】

【表6】

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	B
2	A	A	A	A
3	A	A	B	B
4	B	C	D	D

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の 1 0 % 未満に顕微鏡オーダーの点錆

C 全体の 1 0 % 未満に目視でわかる点錆

D 全体の 1 0 % 以上 3 0 % 未満にやや大きな発錆

E 全体の 3 0 % 以上に著しい発錆、膜ふくれ、はがれ

【 0 1 0 5 】 実施例 7

Sm (C o_{0.69} F e_{0.2} C u_{0.06} Z r_{0.05})_{7.1} の組成をもつインゴットをスタンプミルで平均粒径が 2 5 μ m になるように粗粉碎し、次にジェットミルで平均粒径が 4 . 0 μ m になるように粉碎した。この微粉碎粉に 1 2 k O e の磁場をかけながら金型中で磁場と直角の方向に 1 . 5 t / c m² の力で加圧し圧粉体を得た。この圧粉体を真空中で 1 2 1 5 ° C で 2 時間焼結し、1 1 7 0 ° C で 1 時間溶体化を行い 8 5 0 ° C で 2 h r 時効後徐冷して 8 0 個の焼結体を得た。この焼結体をグラインダーで全面研磨した後、遠心バレル研磨によりコーナーを落とし、洗滌乾燥した。製品の寸法は 2 0 m m φ × 5 m m の円盤状であった。次に容積 2 . 8 リットル深さ 1 5 0 m m の円形ポットに、直径 φ 3 . 0 m m の鋼球を 1 0 k g 投入し、振動数 1 5 0 0 c . p . m . 、振幅 5 m m の振動を加えながら、平均粒度 0 . 3 μ m の T i O₂ 粉末を投入し 5 分間 T i O₂ 粉末と鋼球に振動を加えた。次にあらかじめエポキシ樹脂 (1 0 % M E K 溶液) に浸漬して表

面を樹脂で覆った磁石を 2 0 個投入し、1 5 分間振動させた後取り出した。磁石を 1 2 0 ° C で 2 h r 加熱してエポキシ樹脂を硬化した後、最後に平均粒径 2 m m のクルミ殻 2 k g と共に同じサイズのポットに入れて 5 分間振動させ、表面に残留した余剰の粉末を除去した。

【 0 1 0 6 】 以下同様の方法により各種粉末を被覆した磁石をそれぞれ 2 0 個ずつ作成し、8 5 ° C × 9 0 % R H の条件で耐食性を評価した。その結果を表 7 に示す。

【 0 1 0 7 】 表中、左欄の数字はそれぞれ以下の処理を意味する。

1 - 上記の処理により平均膜厚が 1 0 μ m の皮膜を形成

2 - T i O₂ 粉末に代えて、平均粒径が 1 μ m の F e₂

O₃ 粉末を使用した。

3 - T i O₂ 粉末に代えて、平均粒径が 1 μ m の A l 粉末を使用した。

4 - 焼結磁石に、T i O₂ 添加量が 2 0 % のエポキシ樹脂をスプレー塗装し、1 2 0 ° C で 6 時間キュアして、平均 2 0 μ m の膜厚の塗膜 (単膜) を形成した (比較例) 。

5 - 焼結磁石に皮膜を施さず、そのまま試験した (比較例) 。

【 0 1 0 8 】

【 表 7 】

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	A
2	A	A	A	A
3	A	A	B	B
4	A	A	B	B
5	B	C	D	D

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の 1 0 % 未満に顕微鏡オ

ーダーの点錆

C 全体の 1 0 % 未満に目視でわかる点錆

D 全体の10%以上30%未満にやや大きな発錆

E 全体の30%以上に著しい発錆、膜ふくれ、はがれ

【0109】実施例8

下記の粉末をダイプレス法により成形して25mmφ×20mmφ×10mmのリング状圧粉体を作成した。

(A) Al-2.75wt%Li ガスアトマイズ粉末

平均粒度 20μm

加圧力 2ton/cm²

(B) Mg

ガスアトマイズ粉 10

末

平均粒度 20μm

加圧力 2ton/cm²

【0110】これらの圧粉体をAr雰囲気中で600℃で6時間焼結した。焼結体の密度はいずれも真密度の90%であった。得られた焼結体に次のような被覆処理を各20ヶずつ施した。

①容積2.8リットル、深さ150mmの円形ポットに直径φ3.0mmの鋼球10kg（見掛け密度5kg/リットル）を入れ、平均粒度1μmのTiO₂粉末を20gを投入して5分間振動させて、均一にTiO₂粉末を分散させた。振動の条件は振動数2500c.p.m.、振幅5mmであった。

【0111】次にあらかじめ、樹脂分（エポキシ樹脂97wt%、硬化剤3wt%）10%を溶かしたメチルエチルケトン（MEK）に焼結体に浸漬することにより、樹脂膜で覆った部材を投入してさらに15分間振動を続

けた。これを120℃で2hr加熱した後、破碎したクルミ殻（平均粒度2mm）2kg（見掛け密度1kg/リットル）と共に前記ポットと同サイズのポットに投入し、同様の条件にて5分間振動させることにより、部材表面に残留した余剰の粉末を除去した。膜厚は平均10μmであった。

【0112】②①と同様の方法により約5μmのCu膜を付与した（Cu粉粒径1μm、15g使用）。その後、電解めっきにより平均10μm（最大値14μm、最小値8μm）のNiめっき膜を形成させた。

【0113】③本実施例（Al-Li, Mg）においては、Al, Mgがイオン化傾向がNiより非常に大きいこと、Niめっきを直接施すことができない。そこで水酸化ナトリウム、酸化亜鉛、ロッシェル塩その他微量添加物からなる市販のZn置換溶液に部材を浸漬して表面にZn置換処理（ジンケート処理）を施した後、ワット浴による電解Niめっき処理を実施して平均10μmのNiめっき膜を形成させた。

【0114】④焼結体にスプレー塗装により平均10μmのエポキシ樹脂（カーボンブラック20%添加）皮膜を形成した。

⑤焼結体に皮膜を形成せず、試験した。

表8に、上記A、B、1～5によりそれぞれの皮膜形成法を示した。

【0115】

【表8】

		250hr	500hr	1000hr	1500hr
A	1	A	A	A	B
	2	A	A	A	A
	3	A	E	—	—
	4	B	D	E	—
	5	E	—	—	—
B	1	A	A	A	A
	2	A	A	A	A
	3	A	E	—	—
	4	B	D	E	—
	5	E	—	—	—

試験条件：それぞれ20個を85℃×90%RH放置

チェック項目：外観

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の10%未満に顕微鏡オーダーの点錆

C 全体の10%未満に目視でわかる点錆

D 全体の10%以上30%未満にやや大きな発錆

E 全体の30%以上に著しい発錆、膜ふくれ、はがれ錆は白粉状のAlもしくはMgの酸化物とみられる

③は、めっき液の残留によると思われる膜はがれが多く見られた。

【0116】実施例9

下記の粉末をダイプレス法により成形して、20mm×20mm×5mmのプレート状圧粉体を作成した。

(A) Fe-0.3%C 電解アニール粉末 (平均粒度50μm)

加圧力 3ton/cm²

(B) Al-1%Si ガスアトマイズ粉末 (平均粒度25μm)

加圧力 3ton/cm²

(A) については真空中で1300℃で6時間、(B) については600℃で6時間焼結した。焼結体の密度は (A) については85%、(B) については90%であった。得られた焼結体に次のような被覆処理を各20ヶずつ施した。

①容積2.8リットル、深さ150mmの円形ポットに直径φ3.0mmの鋼球10kg (見掛け密度5kg/

リットル) を入れ、平均粒度1μmのFe₂O₃粉末を20gを投入して5分間振動させて、均一にFe₂O₃粉末を分散させた。振動の条件は振動数2500c.p.m.、振幅5mmであった。

【0117】次にあらかじめ、樹脂分(エポキシ樹脂97wt%、硬化剤3wt%)10%を溶かしたメチルエチルケトン(MEK)に浸漬することにより、樹脂膜で覆った部材を投入してさらに15分間振動を続けた。これを120℃で2hr加熱した後、破碎したクルミ殻(平均粒度2mm)2kg (見掛け密度1kg/リットル)と共に前記ポットと同サイズのポットに投入し、同様の条件にて5分間振動させることにより、部材表面に残留した余剰の粉末を除去した。膜厚は平均10μmであった。

【0118】②①と同様の方法により約5μmのCu膜を付与した(Cu粉粒径1μm、15g使用)。その後、電解めっきにより平均10μmのNiめっき膜を形成させた。

【0119】③部材をあらかじめ実施例8-③と同様にZn置換処理後、電解めっきにより平均10μmのNiめっき膜を形成させた。

【0120】④スプレー塗装により膜厚が平均10μmのエポキシ樹脂皮膜(TiO₂20%添加)を形成させた。

⑤被覆なし

【0121】以上の処理を施した焼結体に対しJIS腐食試験方法による中性塩水噴霧試験(35℃、5%Na

C 1) を行い、外観観察を行った。結果を表 9 に示す。
表 9 に、上記 A、B、1 ～ 5 によりそれぞれの皮膜形成
法を示した。

【 0 1 2 2 】

【表 9】

		2 4 hr	4 8 hr	1 2 0 hr	2 4 0 hr
A	1	A	A	C	C
	2	A	A	A	A
	3	C	D	E	—
	4	C	E	—	—
	5	E	—	—	—
B	1	A	A	B	C
	2	A	A	A	A
	3	C	D	E	—
	4	B	C	E	—
	5	E	—	—	—

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の 1 0 % 未満に顕微鏡オ
ーダーの点錆

C 全体の 1 0 % 未満に目視でわかる点錆

D 全体の 1 0 % 以上 3 0 % 未満にやや大きな発錆

E 全体の 3 0 % 以上に著しい発錆、膜ふくれ、はがれ
A、B 共に ③ についてはめっき膜に多数のふくれが生じ
た。

【 0 1 2 3 】 実施例 1 0

下記非金属材料 A ～ B を作成した。

A. N i - Z n フェライト焼結体 (密度 - 真密度に対
して 9 8 %) を下記の原料を混合し、圧粉し、焼結して得
た。N i O : F e₂ O₃ : Z n O = 2 0 : 5 0 : 3 0

(モル比)。焼結体を切断し、研磨して 1 5 m m × 1 5
m m × 5 m m のブロックを得た。

B. S r フェライト焼結体 (密度 - 真密度に対して 9 8
%) を下記の原料を混合し、圧粉し、焼結して得た。S
r C O₃ : F e₂ O₃ = 1 : 5 . 9 (モル比)。焼結体
を切断し、研磨して 1 5 m m Φ × 4 m m の円柱を得た。

【 0 1 2 4 】 これらの非金属材料 A、B に次の皮膜処理
を施した。

① 実施例 8 と同様の処理により T i O₂ 皮膜を形成し
た。(図 1 0、A - ①、B - ①)

② エポキシ樹脂 (T i O₂ 2 0 % 添加) をスプレー塗装 50

した。(図 1 0、A - ②、B - ②)

処理後切断して顕微鏡により非金属材料上の膜厚分布状
態を観察した。結果を図 1 0 に示す。図より本発明法 ①
の方が、コーナー部でのつき回りが薄く従来法 ② より均
一な塗装が可能であることがわかる。

【 0 1 2 5 】 実施例 1 1

直径 4 0 m m、肉厚 2 m m の半球状おわん型のプラスチ
ック部材を金型成形した。容積 2 . 8 リットル、深さ 1
5 0 m m の円形ポットに直径 φ 3 . 0 m m の鋼球を 1 0
k g 入れ、平均粒度 1 μ m の C u 粉末を 1 0 g 投入して
5 分間振動させた。次に部材の全面に M E K を吹きつ
け、表面を粘着性とし、前記ポット内に投じて 1 5 分間
振動を続けた。その後プラスチック部材を取り出して 5
0 ° C で 2 h r 加熱した後、破碎したクルミ殻 (粒径 2 m
m) 2 k g と共に同サイズの別のポットに入れ、5 分間
振動させ、部材表面の残留粉をとり除いた。

【 0 1 2 6 】 これにより部材表面に約 4 μ m の C u 層が
形成され、処理前には無限大であった表面の抵抗値が
0 . 2 ～ 0 . 5 Ω / c m に減少し、通常のワット浴を用
いて容易に N i めっきを施すことができた。めっき後の
部材にテープ試験を行ったが、剥離は起こらなかった。

【 0 1 2 7 】 実施例 1 2

図 1 1 に示す心臓型のガラス片 1 0 0 個に下記の処理を
施した。

① 5 % M E K 溶液を樹脂として使用したほかは実施例 8 と同じ処理により、平均粒径 $1 \mu\text{m}$ の金粉 5 g を投入して 1 5 分振動させたところ、約 $2 \mu\text{m}$ の美しい金皮覆が施された。テープ試験で剥離はみられなかった。

【 0 1 2 8 】 ② 実施例 8 と同様の処理により、平均粒径 $1 \mu\text{m}$ の C u 粉 2 0 g を投入して 1 5 分振動させることにより、約 $1 0 \mu\text{m}$ の C u 皮覆を施した。これにより、部材の表面抵抗は $0.2 \sim 0.5 \Omega / \text{cm}$ となり、充分電気めっきが可能な状態となった。引き続き電解めっきにより約 $2 \mu\text{m}$ の金めっきを施すことにより、光沢のある極めて美しい表面が得られた。

【 0 1 2 9 】 実施例 1 3

N d_{13.8} D y_{0.4} F e_{78.2} B_{7.6} の組成をもつインゴットをスタンプミルで平均粒径が $2 0 \mu\text{m}$ になるように粗粉碎し、次にジェットミルで平均粒径が $3.0 \mu\text{m}$ になるように微粉碎粉に $1 2 \text{ k O e}$ の磁場をかけながら金型中で磁場と直角の方向に $1.5 \text{ t} / \text{cm}^2$ の力で加圧し圧粉体を得た。この圧粉体を真空中で $1 1 0 0^\circ\text{C}$ で 2 時間焼結した後、 $6 5 0^\circ\text{C}$ で 1 時間時効処理して 6 0 個の焼結体を得た。この焼結体をグラインダーで全面研磨した後、遠心バレル研磨によりコーナーを落とした後、洗滌乾燥した。製品の寸法は $2 0 \text{ mm} \phi \times 5 \text{ mm}$ の円盤状

であった。次に容積 2.8 リットル深さ $1 5 0 \text{ mm}$ の円形ポットに、直径 $\phi 3.0 \text{ mm}$ の鋼球を $1 0 \text{ kg}$ 投入し、振動数 $2 5 0 0 \text{ c. p. m.}$ 、振幅 5 mm の振動を加えながら、平均粒度 $1 \mu\text{m}$ のスズ粉末 $3 0 \text{ g}$ を投入し 5 分間スズ粉末と鋼球に振動を加えた。次にあらかじめ 5 % パラフィン M E K 溶液に浸漬して表面を樹脂で覆った磁石を 2 0 個投入し、1 5 分間振動させた後取り出した。最後に平均粒径 2 mm のクルミ殻片 2 kg と共に同じサイズのポットに入れて 5 分間振動させ、表面に残留した余剰の粉末を除去した。

【 0 1 3 0 】 次に部材を $3 0 0^\circ\text{C}$ で 4 時間真空中で加熱して取り出し、 $8 5^\circ\text{C} \times 9 0 \% \text{ RH}$ の条件で耐食性を評価した。その結果を表 1 0 に示す

【 0 1 3 1 】 表の左欄の数字は以下の処理を意味する。

1 スズ処理品 (平均膜厚 $1 0 \mu\text{m}$)

2 スプレー塗装 (エポキシ樹脂 ; T i O₂ 2 0 % 添加)

平均膜厚 $1 0 \mu\text{m}$

3 処理なし

【 0 1 3 2 】

【 表 1 0 】

	2 5 0 hr	5 0 0 hr	1 0 0 0 hr	1 5 0 0 hr
1	A	A	A	A
2	C	E	—	—
3	E	—	—	—

試験条件 : $8 5^\circ\text{C} \times 9 0 \% \text{ RH}$ 放置

チェック項

目 : 外観

判定基準 A 全数全く発錆なし

B 巨視的には発錆なし。全体の 1 0 % 未満に顕微鏡オーダーの点錆

C 全体の 1 0 % 未満に目視でわかる点錆

D 全体の 1 0 % 以上 3 0 % 未満にやや大きな発錆

E 全体の 3 0 % 以上に著しい発錆、膜ふくれ、はがれ

【 0 1 3 3 】

【 発明の効果 】 以上説明したように本発明は簡便な方法により、耐食性、密着性にすぐれた粉体皮膜を各種部材に施すことができるので、従来よりも粉体皮膜の適用範囲が拡大される。さらに、従来樹脂塗装では十分な耐食性が得られない被処理材に本発明法を適用することによって優れた耐食性を得ることができる。

【 図面の簡単な説明 】

【 図 1 】 本発明による攪拌をアームにより行う実施例を示す図である。

【 図 2 】 本発明による攪拌を羽により行う実施例を示す

図である。

【 図 3 】 本発明による攪拌を回転容器の回転により行う実施例を示す図である。

【 図 4 】 本発明による攪拌を円筒容器の回転により行う実施例を示す図である。

【 図 5 】 本発明による攪拌を円筒容器の揺動により行う実施例を示す図である。

【 図 6 】 本発明による攪拌を容器を回転軸の回りに回転させて行う実施例を示す図である。

【 図 7 】 本発明による振動をポットの加振により行う実施例を示す図である。

【 図 8 】 本発明による振動をといの加振により行う実施例を示す図である。

【 図 9 】 といの実施例を示す図である。

【 図 1 0 】 皮膜の付き回りを示す図である。

【 図 1 1 】 被処理部材の図である。

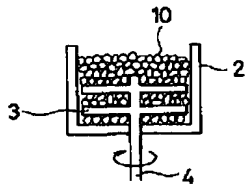
【 図 1 2 】 皮膜中の T i O₂ 粒子の構造を示す電子顕微鏡写真である。

【 符号の説明 】

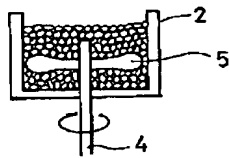
- 2 容器
3 アーム
4 回転軸
5 羽根
6 ローラー

- 8 加振器
10 皮膜形成混合物
20 とい
22 ふるい
24 皮膜形成媒体

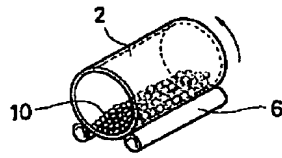
【図 1】



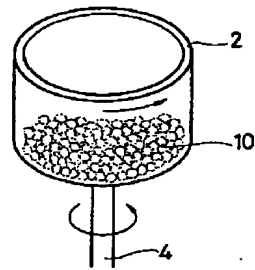
【図 2】



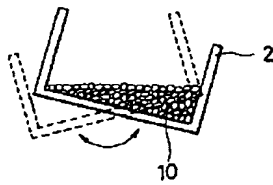
【図 3】



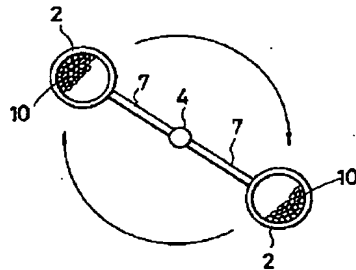
【図 4】



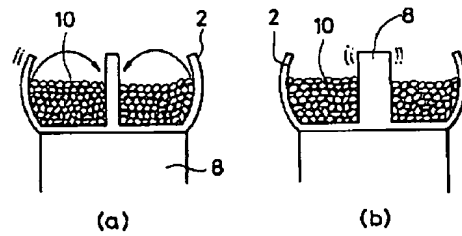
【図 5】



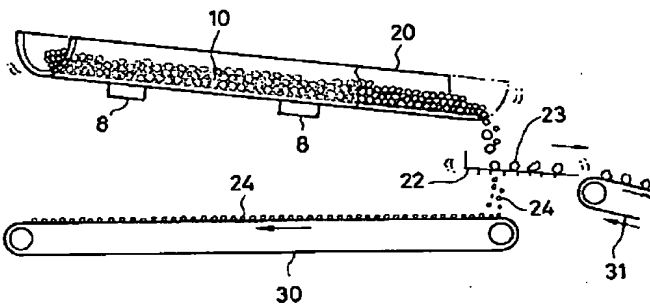
【図 6】



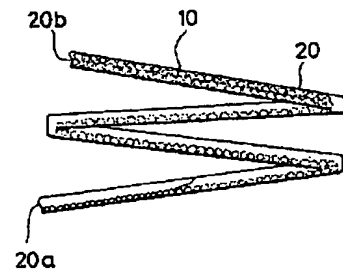
【図 7】



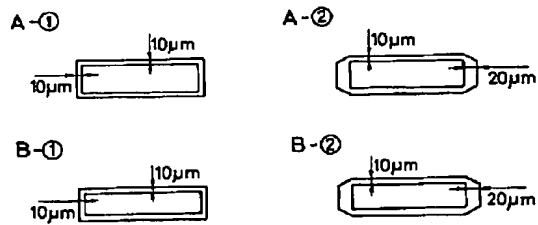
【図 8】



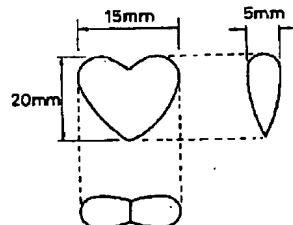
【図 9】



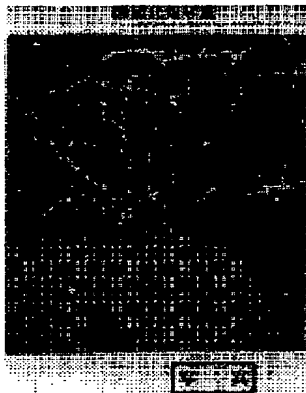
【図 10】



【図 11】



【図12】



フロントページの続き

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